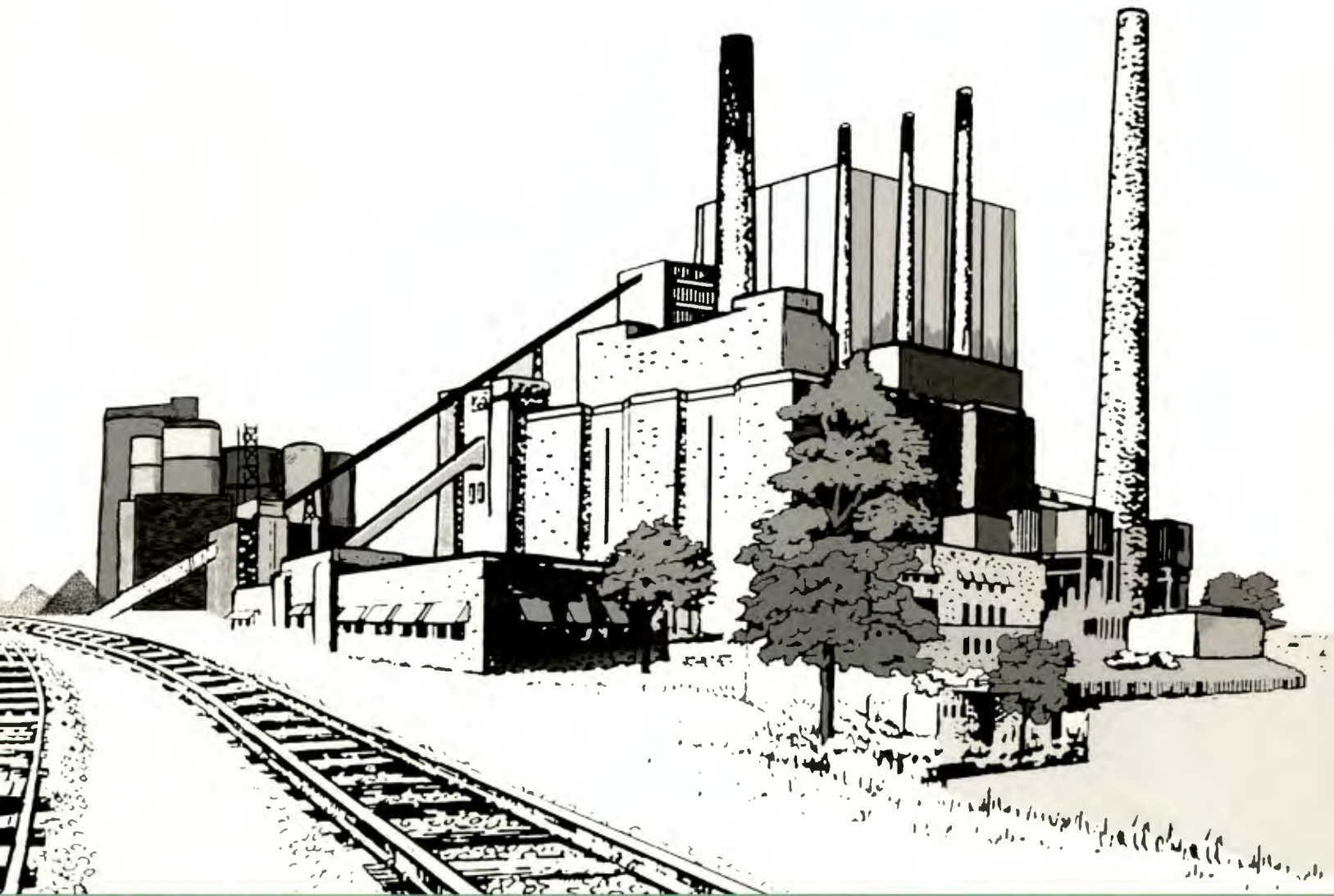# Indiana Limestones and Dolomites for Flue Gas Desulfurization

Indiana Geological Survey Special Report 67

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Indiana Limestones and Dolomites for Flue Gas Desulfurization

By Nelson R. Shaffer and Robert Sadowski

Indiana University
Indiana Geological Survey Special Report 67

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By Nelson R. Shaffer and Robert Sadowski

ABSTRACT

Required reductions of sulfur compounds from gas streams, called "flue gas desulfurization," as mandated by the Clean Air Act Amendments of 1990, encouraged installation of wet limestone scrubbers at many coal-fired electricity-generating plants. Because Indiana has large deposits of limestone—the major consumable alkaline raw material for scrubbers—the state can meet an expected demand of several million tons per year.

Limestone from varying limestone units behaves quite differently when used as scrubbing agents, therefore thorough knowledge of the rock units is essential. The location of suitable limestones close to the generating plants is also important. Optimizing the fit between geological characteristics of limestones and prospective scrubber systems will greatly improve planning and should result in lower overall costs for operation.

Models developed by electric utilities to predict flue gas desulfurization system operations require geologic and geochemical data that are often unvailable from standard analyses. To provide essential geologic and geochemical details of Indiana scrubber stone raw materials and apply these data to the FGD-PRISM model, several hundred limestone samples from more than 30 active quarries were collected and their physical properties determined. Grindability values ranged from 7.2 to 21.7 for 50 selected samples. Acid-insoluble residues ranged from less than 1 percent to 55 percent. Dissolution rates, as an index of reactivity, varied over two orders of magnitude for the selected set of samples. These data, and chemical analyses and calcium-to-magnesium ratios, were entered into a generic scrubber model to determine rates of stone use and scrubber efficiency for various stone.

Removal of sulfur dioxide was projected by this model to range from 89 percent to 98 percent and stone utilization rates were from 91 percent to 93 percent. Excellent sources of scrubber stone were found in Mississippian age rocks in central and southern Indiana. Rocks of the Paoli, Ste. Genevieve, and Salem Limestones (Mississippian) were especially efficient; however, even small amounts of dolomite, clay minerals, and quartz diminished a stone's usefulness for flue gas desulfurization.

Residues of the FGD process such as scale can form in pipes, filters, and other parts of the system. Residues can be reduced with certain additives. The formation of scale can adversely affect scrubber operations. Sulfite and sulfate residue from FGD are now used in a number of applications, usually large-scale agriculture or construction projects. Work on high- value uses deserves attention as does the ability of the residue to sequester certain metals.

INTRODUCTION

Indiana coal production decreased during the early 1990s, in part because of restrictions on sulfur emissions from coal-fired generating plants imposed by the Federal Clean Air Act Amendments of 1990. However, coal consumption continued to climb because electric power utilities imported lower-sulfur coal from other states to replace the relatively higher-sulfur Indiana coal (fig. 1). Sulfur dioxide (SO_2) emissions from burning sulfur-bearing coals can be reduced by cleaning or "scrubbing" stack gases using finely crushed limestone as the scrubbing agent. If sulfur emissions can be cleaned effectively, Indiana coal can continue to supply energy for the region's electric needs and be competitive with imported coal.

Indiana contains abundant deposits of limestone and dolomite carbonate rocks, some of which afford good raw material for wet-scrubbing, the most common and best proven technique of flue gas desulfurization (FGD) (Baviello, 1982). The initial costs of designing and constructing FGD systems are substantial, and operating expenses through the life of the systems contribute to increased utility rates. To meet regulations, some companies have resorted to alternative fuels or blending local coals with lower-sulfur western or Appalachian coals. Optimizing scrubber selection and performance should help Indiana coal remain an environmentally sound and economically attractive fuel choice.

Although abundant carbonate rocks occur in Indiana, details of their suitability to scrubbing systems have received little attention and almost no attempts have been made to match details of stone resources available in Indiana with the needs of various utility scrubber systems. Optimizing the fit between geological characteristics of the existing stones and potential new scrubber systems should allow for greatly enhanced efficiencies of FGD systems and consequent cost reductions, thus making substitution by non-Indiana fuels less attractive.

Electric utilities have developed computer models to predict FGD system operations, for example, the FGD PRISM model of the Electric Power Research Institute (EPRI, 1991). These models required geologic data that were made available through a cooperative effort between the Indiana Department of Commerce, the Indiana Geological Survey (IGS), the Indianapolis Power & Light Company (IP&L), and the Indiana Mineral Aggregates Association (IMAA).

Statement of problem

Required reductions of sulfur compounds from gas streams, mandated by the implementation of the Clean Air Act Amendments of 1990, have encouraged installation of wet limestone scrubbers at many generating plants. More stringent requirements that took effect in 2000 are necessitating even more extensive use of such scrubbers. The Clean Air Act Amendments of 1990 (Bill S.160, Sections 404 and 405) stipulated reductions in sulfur dioxide (SO_2) emissions by electricity producers to no more than 2.5 pounds per million Btu in Phase I of that law and further reductions to 1.2 pounds SO_2 under Phase II, which began in 2000. Indiana has sufficient deposits of limestone—the major consumable alkaline raw material for scrubbers—to meet an expected demand of greater than 2.0 million tons per year. Limestones are not all the same, however, and stones from various geologic units behave quite differently when used as scrubbing agents under the varied conditions encountered in actual practice. Better decisions about FGD scrubber
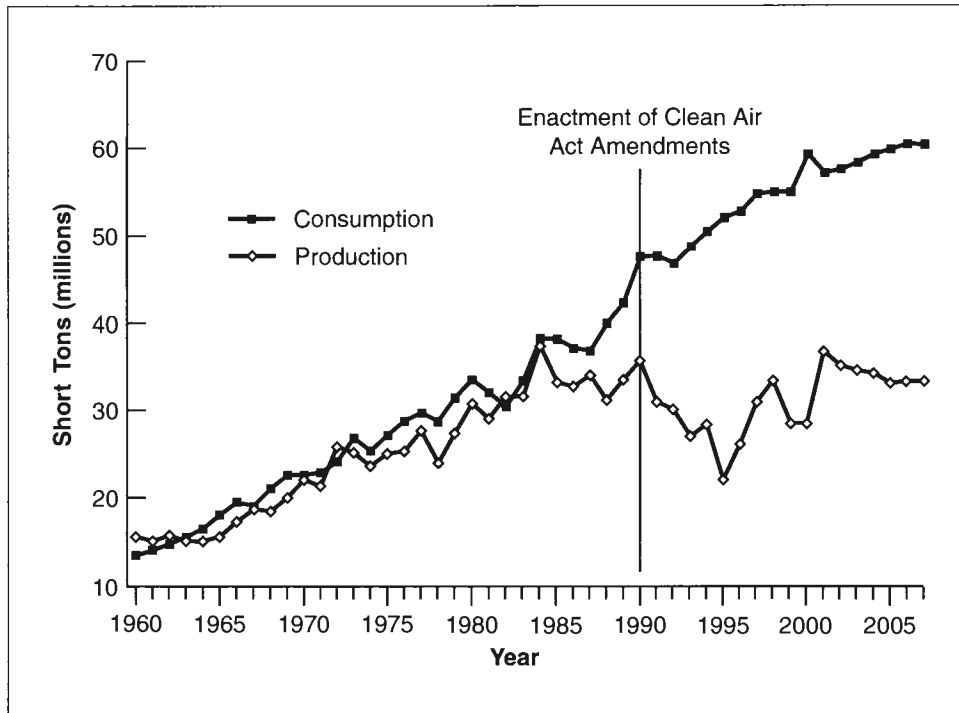
Figure 1. Graph showing Indiana coal production and consumption from 1960 through 2007.

details could be made given a more thorough understanding of the deposits that contain the limestones and dolomites most effective as scrubbing agents and knowing the location of stone reserves nearest to power-generating facilities.

It has long been known that limestone reacts with sulfur in the air. Limestone buildings remove sulfur from the air (Braun and Wilson, 1970). Atmospheric sulfur reacts with the calcium in limestone or marble to form gypsum crystals. Rainwater washes the readily soluble gypsum from the surface, but some does migrate into the stone. Removal of atmospheric sulfur ranged from 45 to 59 percent in their experience. Malaga-Starzec and others (2004) reported that calcareous dimension stone deterioration is dependent upon surface chemistry of individual stones. Even under conditions of low temperature and low sulfur concentrations, limestones can extract sulfur from gases.

More than 60 different processes for removing sulfur oxides (SO_x) and nitrous oxides (NO_x) compounds from flue gas appear in patent literature (Neville, 1977). The most commonly used methods in the United States are wet scrubbing with limestone or lime, which accounted for 86 per-

cent of scrubbers in use to 1981 (Baviello, 1982). Crowe (1974) suggested that use of limestone for scrubbing will be considerable and estimated that a 1,000-MW station would require 300,000 tons of limestone each year. Wet scrubbing of SO_2 using limestone slurries is the most commonly used technique; at present, 20 scrubber units exist, and additional scrubbers are being planned to bring Indiana's existing coal-fired power plants into compliance with provisions of the Clean Air Act amendments that go into force in the year 2010.

A great amount of theoretical and experimental work has gone before practical FGD systems. Olausson and others (1993) reviewed major models for SO_2 sorption by limestone slurries. Previous simulator models such as the Chemistry and Process Engineering Simulator (CAPES) or the FGD PRISM methods suggested that the PRISM method (EPRI, 1991) is faster and more stable than other models. They did note that changes in chemical details such as magnesium or chlorine concentrations complicate model results. Considerable unpublished or contract reports also exist for specific operations of various kinds including dry limestone injection of calcined limestone or lime (Munoz-Guillena and others, 1996; Borgwardt, 1970) or pressurized fluid-

ized bed combustion (Snyder and others, 1978; Liang and others, 1991; Yrjas and others, 1995; Chin and others, 2005), but in this report we will concentrate on wet scrubbers that use limestones.

Limestone scrubbing can remove 75 to 90 percent of sulfur oxides from power plant emissions (Baviello, 1982). Because of their advantages—proven technology, relative ease of retrofitting, and widespread availability of limestones—many limestone-based scrubbers have been installed in systems designed to burn coal (EPA, 1974; Berza and Lynn, 1975; Baviello, 1982). High-calcium limestones are the best material for scrubbing SO_2, but early research showed that not all pure limestones were suitably active (Harvey, 1970). Different limestones, even those having similar overall chemical compositions, behave quite differently in large-scale scrubbing use. Some carbonates fail to react completely, resulting in inefficiencies such as excessive waste production. Other limestones form intermediate reaction compounds that can build up in filters, while others are known to cause excessive abrasion to equipment or to make dewatering difficult. Carbonates used in other desulfurization processes, such as fluidized-bed combustion, dry injection, dual alkali, and other methods, may require various stone properties. To make the best use of Indiana's abundant limestone and coal resources, it is necessary to discern the stones that are best suited for scrubbing and to know geographic and geologic details of units containing stone with proper properties.

Potter (1969) demonstrated that the sulfur dioxide sorption capacity of limestones ranged from 17.3 to 66.4 $SO_2/100$ g. He noted that well-crystallized Iceland spar calcite gave the lowest values and oolites and chalks gave the highest values. Variations of 5 to 43 percent reduction were found by Attig (1970), and even limestones used in fluidized-bed desulfurization showed marked differences (Bodin and Frazier, 1985; Ciambelli and others, 1985) that related to physical properties. Good correlations, however, were noted between SO_2 sorption capacity and pore volumes (Potter, 1969) in wet scrubbing. But tests in continuous equipment have indicated that performances comparable with chalk can be obtained with ordinary limestones (Slack, 1971).

Pore structure is known to affect SO_x reactions with limestone (Hartman and Coughlin, 1974; Cheng and others, 2004) or lime (Siagi and others, 2007).

Borgwardt and Harvey (1972) proved that pore size and geometry of raw rock are important factors in the ability of a stone to absorb SO_2 and account for some of the 15-fold differences in sorptive capacities of different stones. They found that small pores result in faster reaction rates but lower total removal, while stones with larger pores absorbed more SO_2 and specific reaction rates increased with surface area. Harvey (1970) had previously related petrography of stones with their ability to absorb SO_2 from flue gases and found that pore size and sodium (Na) content could be used to predict performance behavior. Presumably, higher Na values resulted from more fluid inclusions or other imperfections that contain brines. Unfortunately, limestones having very similar chemical compositions do not necessarily behave the same in FGD systems of varied design (Harrington and others, 1968). Recent research has indicated that textural features such as pore size, perfection of crystals, and particle size have considerable importance in predicting the ability of a particular limestone to react with SO_2.

Similar results were reported by Harvey and Steinmetz (1971) and Harvey and others (1972) who found that pores between 2 and 16 μ have the most influence on sorptive capacity of limestones. They also noted a positive relationship between Na and sorptive ability and that marls and chalks, both fine, porous soft carbonates, showed the best SO_x capturing capabilities. Carrying this work further, Harvey and others (1974) reported additional encouraging data on impure marls and chalks and suggested that oolitic aragonite, pelecypod shells, and carbonate industrial-waste sludges could be used to effectively remove SO_x from stack gases. The large surface areas, fine grain sizes, and lack of crystallinity of such rocks seemed to account for their superior ability to scavenge sulfur oxides.

Even biological processes have been investigated as sulfur removal technologies (Sublette and Gwozdz, 1991; Grootaerd, 1998; Philip and Deshusses, 2003). Most of these have focused upon using sulfite-reducing bacteria (SRB) in concert with waste treatment. A number of bioreactor designs have been tested (Selvaraj and others, 1997; Lens and others, 2003). Li and others (2007) noted that microorganisms promoted dissolution of limestone about tenfold. A pretreatment by, or addition of, appropriate organisms might well improve limestone use by improving release of calcium ions (Ca^{2+}) and

by promoting porosity or by forming other nano-architectural details that could enhance SO_x reactions of stone particles.

It is well established that high-calcium limestones generally work better in wet scrubbing. Basic chemical analyses of any candidate stone is of major importance. It is important to know the content of available magnesium (Mg). Certain processes work best with stone that contains up to approximately 5 percent of available Mg, especially when Mg is present as intercrystalline substitutions. Magnesium in the crystal structure of the mineral dolomite (in which Mg ranges up to 48 percent MgO) is not reactive, and therefore not available. Furthermore, silicon (Si), aluminum (Al), and iron (Fe) content of candidate scrubber stones hinder the reactivity of the carbonate. Some evidence exists that stones having considerable Na perform better than those with lower Na. Trace element determination should also provide data useful in predicting scrubber performance.

Physical, petrologic, and chemical properties are critical to the practical use of carbonate scrubber stones. Hardness is a very important physical property because it helps determine ease of size reduction or grindability. Any stone has to be comminuted to generally less than 325 mesh (0.0017 in, 45 μm) and very hard stones require excessive energy to grind. American Society for Testing and Materials and the Electric Power Research Institute (EPRI) have developed methods to determine empirical rankings of grindability.

The particle size of limestone in the FGD slurry is very important in determining rate and completeness of reactivity. Finer particles have higher surface areas available for reaction. Early studies (for example, Chang and Dempsey, 1982) showed that finer sizes (85% passing 325 mesh) of limestones were most economical for SO_2 removal. Further grinding had little effect. Size is also important for dry injection (Hartman and others, 1978; Kenakkala and others, 1991; Hepola, 1992). Rogers and others (1999) reported on advances in fine grinding and gave estimates of power requirements and costs for grinding FGD materials. As noted earlier, porosity and other texture details also affect stone performance, but the ease of size reduction or grindability is an important factor in determining optimum stones for SO_2 removal. Shih and others (2000) noted the importance of particle size and BET surface area on dissolution rates thus show-ing the importance of stone grinding on the overall process.

The actual rate of dissolution and completeness with which stones react to remove SO_2, or its reactivity value, is also an important property to consider. EPRI has developed standard techniques to determine reactivity. This value is used along with chemical analyses, Mg availability, grindability, and chemical engineering parameters peculiar to each system in the FGD-PRISM model (EPRI, 1991), which is used to predict stone-scrubbing efficacy. Selected values for these parameters are currently available, but ranges and averages must be established for various geologic units to provide data necessary for using the FGD-PRISM model, thus promoting better stone selection.

Physical properties of water absorption, specific gravity, and acid-insoluble residue, plus detailed petrographic point counts of rock thin sections illustrate the variability of our Indiana stone samples in relation to reactivity values. Poor correlations appear to exist between gross-water absorption or specific gravity and reactivity, and a slight negative correlation exists between insoluble residue and reactivity. Petrographically determined percentages of dolomite, sparry cement, clay, quartz, iron minerals, and porosity showed negative correlations with reactivities. The amount and type of mineral matter can be determined by dissolving and weighing residue for insoluble percentages and then analyzing the insoluble fractions by X-ray diffraction. Additional petrographic information such as limestone types, sizes, cements, textures, fossils, and other constituents gained by polarized light analyses very likely will shed more light on this currently poorly understood mechanism of reactivity. Several of these variables should relate theoretically to reactivity. Some petrographic and physical properties may prove critical for future studies of stones useful to fluidized-bed combustion, gasification, or to other coal uses. Petrographic information, though no panacea, can aid in assessing suitability of limestones for SO_2 scrubbing.

Previous studies

Publications of general research relating to limestone characteristics as applied to scrubbing technology abound. Most of this information was reviewed in the introduction, but four works are especially apropos to this study: Harvey and oth-

ers (1972) reported on limestones from Illinois; Stith and others (1997) presented an overview of potential scrubber stone resources in the Ohio River valley but no analyses were reported; Miller and others (1996) evaluated 25 limestone samples from Pennsylvania for their scrubbing efficiencies; and Shaffer and Krause (1988) presented work about a limited set of limestone analyses from Indiana. They reported values for stone reactivities for the Number 3 scrubber at IP&L, and these data are summarized in Table 1 and also in Appendix C of a previous report by Shaffer and Sadowski (2000). Unfortunately the values were not directly applicable to all scrubbing systems. A report by the Electric Power Research Institute (EPRI, 1991) set forth detailed standard procedures to determine dissolution rates of limestones that could be used for various scrubber systems. Details of these procedures are found in Appendix B of Shaffer and Sadowski (2000).

Table 1. Summary of physical properties of potential scrubber stone samples from previous study of Shaffer and Krause (1988)

Property	Range	Average
Specific gravity	2.00–2.71	2.64
Absorption	0.4–11.8	1.46
Insoluble residue	0.3–35.4	6.81
Hardness (Bond Work Index)	6.6–12.3	10.5
Relative reactivity index	0.4–5.0	3.4

Several studies have assessed general considerations for scrubber stone. Jones (1991) and Jones (1993) looked at overall compliance strategies especially with respect to stone qualities. Miller and others (1993) provide an extensive bibliography of reports about industrial minerals used for FGD. EPRI (1990, 1991, 1994, 1995) released a number of guidelines for flue gas scrubbing to which the reader may refer. While a few instances of Mg-rich stones were reported (for example, Telesz, 1993), most workers stress the importance of high-calcium limestones that are low in impurities.

Bhagwat (1985), Cobb and Dever (1991), and Stith and others (1997) presented general outlines of geology and economic features particular to the midwestern United States. The Pure Air wet scrubbing project in Lake County (Clean Coal Today, 1994) along with practical experience at several generating plants prove that adequate quantities of suitable scrubber stone can be obtained in the Midwest.

Objectives

The primary objective of this work was to improve the competitiveness of sulfur-bearing Indiana coals by optimizing FGD processes at electric-generating plants. Wet scrubbing of stack gases can meet current sulfur emission regulations and is a proven technology. It is especially effective as a retrofit system and can be tailored to produce gypsum as a salable byproduct. Several units are on line in the Midwest and have performed well. More wet limestone units will be installed in the Midwest in the next few years. Improved selection and operation of such systems should result from analyzing new geological information about carbonate rocks used in FGD and applying those data to the FGD-PRISM model.

Improved scrubbing will promote continued, even increased, use of Indiana coal. Knowledge of stone characteristics helps to optimize performance of existing wet scrubbers and helps to diagnose potential ancillary problems of fouling, excess wear, byproduct potential, or disposal difficulties. Model estimates have been used to improve procurement procedures by allowing better matches of coal properties and scrubber stone details. This study provides data that can be used in selecting specific FGD systems for new installations. All these factors should improve overall efficiency of energy use and electric production while meeting environmental strictures. New data should support expanded use of Indiana coal and limestone by utilities in Indiana and surrounding areas.

Procedures

Carbonate rock samples representative of Indiana's various carbonate lithologies on a statewide basis were selected, collected, and characterized (Appendix A in Shaffer and Sadowski, 2000). Approximately 50 promising stones were selected with advice and assistance from the Indiana Mineral Aggregates Association and its member companies.

The Electric Power Research Institute developed standard, widely accepted methods to determine limestone properties important to FGD efficiency.

Details of these testing procedures are given in Appendix B of Shaffer and Sadowski (2000).

Carbonate rock samples were geologically described, then prepared and analyzed to determine physical properties of specific gravity, porosity, and amount and characteristics of acid-insoluble materials. Grindability or ease of size reduction is an empirical test that requires specific equipment. The 50 samples analyzed for reactivity underwent grindability measurements following EPRI techniques. Geologic information along with reactivity, Mg availability, and grindability data were entered into the FGD-PRISM model for a specific case as determined by IP&L. We present a general ranking of stone for efficiency in that specific system.

Major oxide geochemical analyses were performed by inductively coupled plasma (ICP) spectrometer analysis and ion chromatograph techniques. Magnesium availability and limestone dissolution or reactivity were measured using EPRI/Radium techniques for 56 samples.

GEOLOGIC SETTING

General geology

The midwestern United States contains large deposits of carbonate rocks (fig. 2A). Limestones having high calcium and limited Mg content are required for wet FGD. Indiana abounds in such carbonates (fig. 2B), and carbonate lithologies make up much of the bedrock system throughout the state (fig. 3). Rocks suited to scrubber applications occur within the Silurian Wabash Formation; the Devonian rocks of the Muscatatuck Group; and in the Mississippian Sanders, Blue River, West Baden, and Stephensport Groups (fig. 4). Bedrock units crop out in belts of varying widths that trend northwest-southeast. Details of topography exemplify the complexities of actual outcrop patterns. Descriptions of Indiana's geology are summarized by Hill (1986a, b), Camp and Richardson (1999), and Hall (1999). A number of large faults, or breaks in the rocks, are known, and other smaller or still hidden faults probably exist that can affect outcrop patterns and even thicknesses of units. Faults, while important to many processes, are not known to affect existing quarries except at one site at the Kentland cryptoexplosive structure in Newton County where rocks from the Ordovician Period are quarried.

Limestone quarries exist in many counties of Indiana (fig. 5) where bedrock is of sufficient quality, markets for stone exist, and conditions permit mining. Unpublished data on quarries, outcrops, and cores are recorded as memorandum reports of the Coal and Industrial Minerals Section at the Indiana Geological Survey. These reports, which contain details of location, rock chemistry, rock petrology, unit thicknesses, physical properties, and other data, were studied to determine the locations most likely to produce scrubber-quality stones. Rock descriptions and chemical data have been published by Rooney (1970), Rooney and Carr (1975), Ault and Carr (1978), Carr and others (1978), Ault and Moore (1980), Shaffer and others (1982), Shaffer and Krause (1988), and Ennis (1994, 1995). The most promising units are in the west-central to south-central part of the state (figs. 2B and 4). The bedrock in the north and east tends to be dolomitic, which as noted earlier, mitigates against performance as a scrubbing agent. Our efforts were focused upon limestone-rich units such as the Paoli, Ste. Genevieve, and Salem Limestones of Mississippian age, or the North Vernon and Jeffersonville Limestones of Devonian age, and the Louisville Limestone of Silurian age. A few tests were made of limestone units in the Wabash Formation (Silurian) and the West Baden Group (Mississippian).

Long after lithification and erosion of the bedrock surface, large continental glaciers deposited varied thicknesses of unconsolidated sediments throughout most of Indiana during the Ice Age (Pleistocene Epoch). The map in Figure 3 shows the extent of these deposits, which cover bedrock north of the boundaries shown. Thicknesses of the drift cover vary, but can exceed 450 ft (Ault, 1993a). Quarries are developed mainly where glacial material that covers good bedrock deposits is thin or absent. Quarries, however, can exist even where glacial deposits are relatively thick, if economic deposits of sand and gravel overlie the limestone and can be removed first.

Limestone mines

In 2006, limestone was mined from 90 crushed stone quarries and 19 dimension stone quarries in 43 of Indiana's 92 counties (figs. 5 and 6). General distribution of suitable limestones follows the bedrock outcrop trend except for a locale that trends from Putnam County to the Ohio River in Harrison County from which rocks of the Blue River
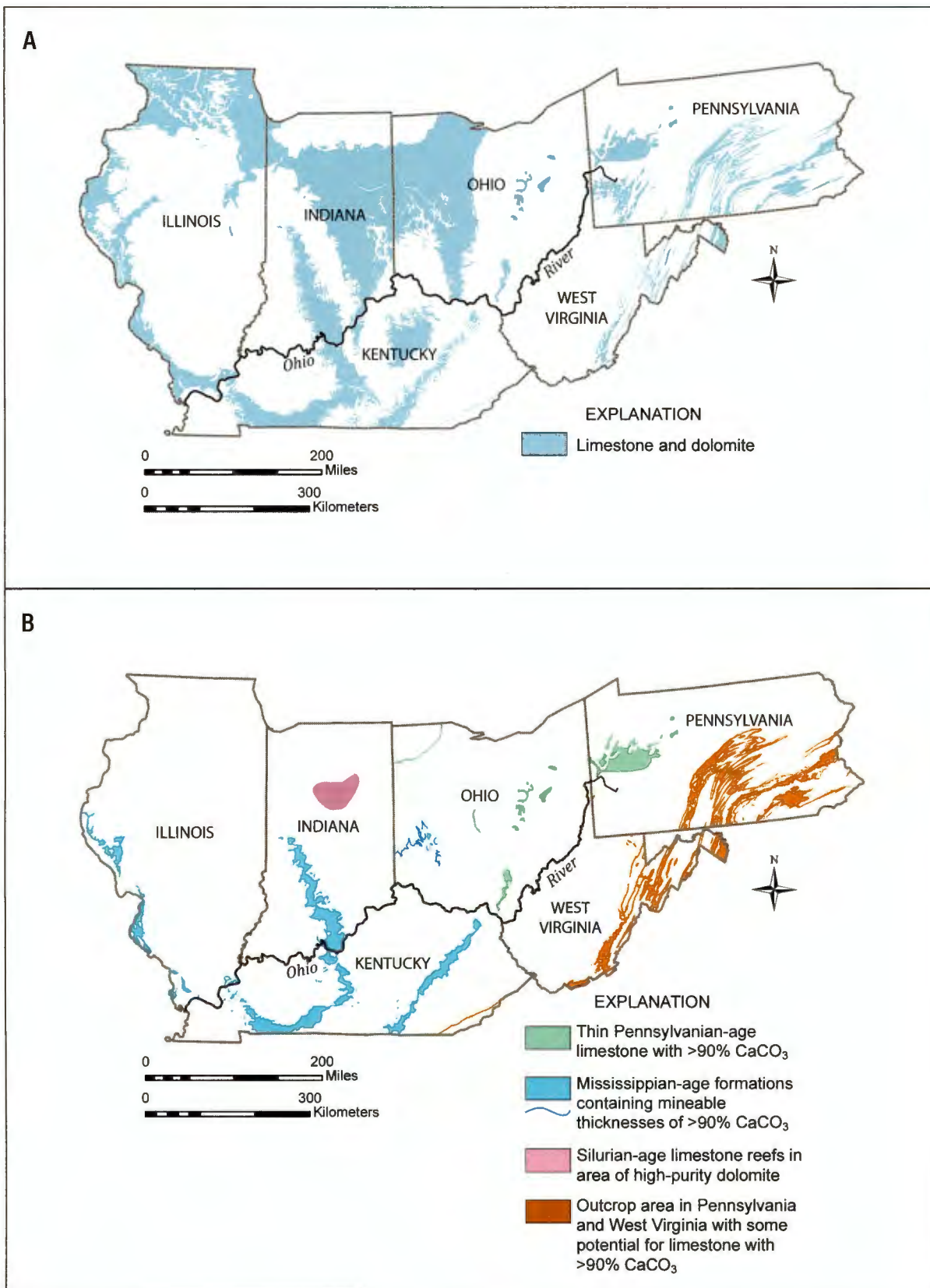
Figure 2. Maps of six-state area showing: A) Outcrop area of limestone and dolomite in the Ohio River Valley; B) Outcrop/subcrop area of formations containing mineable thicknesses of limestone having more than 90 percent calcium carbonate ($CaCO_3$). From Stith and others (1997).
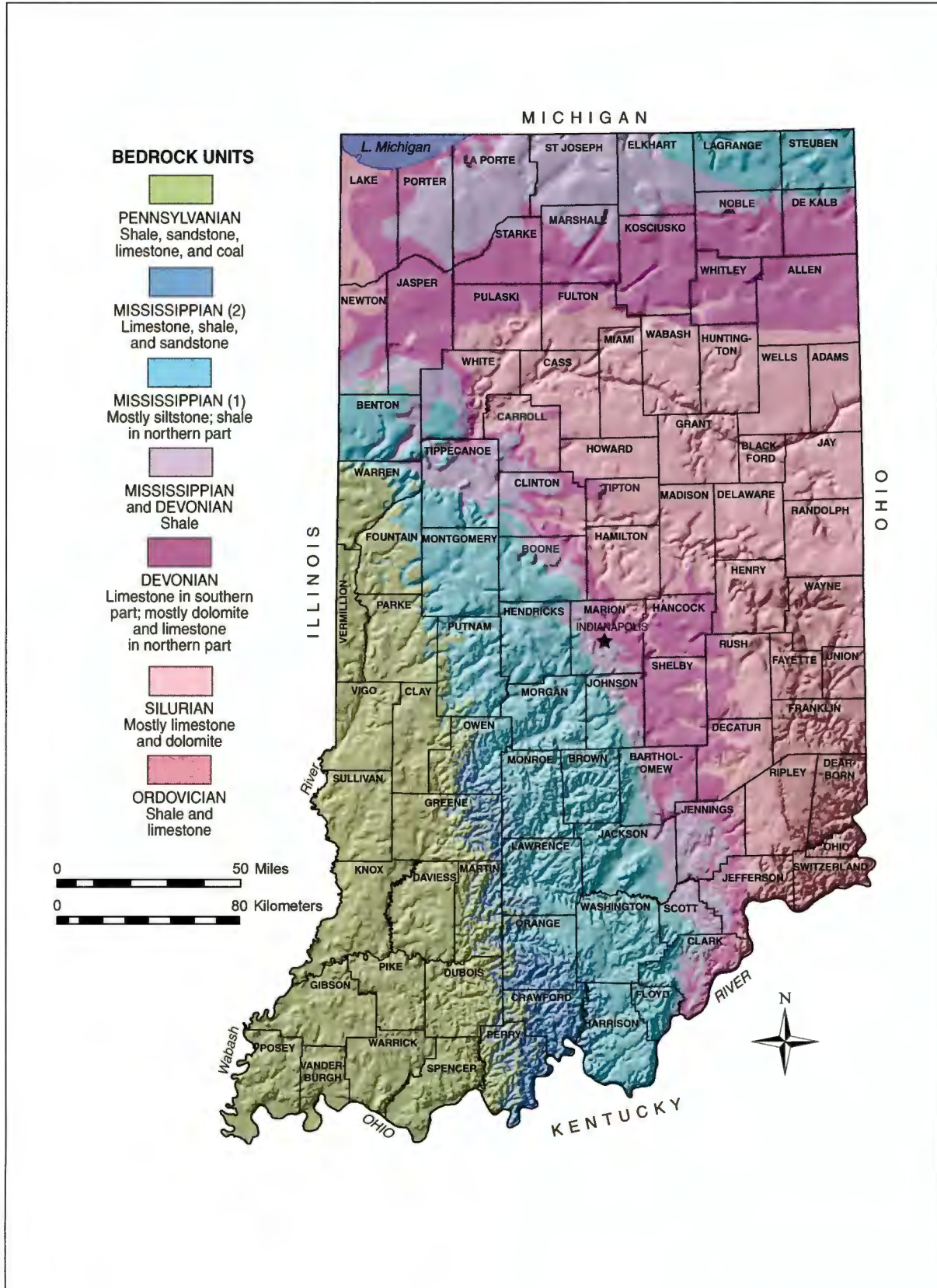
Figure 3. Map of Indiana showing bedrock geology. From Thompson and Sowder (2005).

AGE (millions of years)	PERIOD	THICKNESS (feet)	LITHOLOGY	ROCK UNIT		
				SIGNIFICANT MEMBER	FORMATION	GROUP
318	MISSISSIPPIAN				*southwest* Grove Church Sh.	
					Kinkaid Ls.	
			— Negli Creek Ls.		Degonia Fm.	*south-central* Tobinsport Fm.
		30 to 300			Clore Fm.	
					Palestine Fm.	
			— Leopold Ls.		Menard Ls.	Branchville Fm.
					Waltersburg Fm.	
					Vienna Ls. *southwest and south-central*	
					Tar Springs Fm.	
		120 to 200			Glen Dean Ls.	Stephensport
					Hardinsburg Fm.	
					Haney Ls.	
					Big Clifty Fm.	
					Beech Creek Ls.	
		100 to 250			Cypress Fm. | Elwren Fm.	West Baden
					Reelsville Ls.	
					Sample Fm.	
					Beaver Bend Ls.	
					Bethel Fm.	
		250 to 650			Paoli Ls.	Blue River
					Ste. Genevieve Ls.	
					St. Louis Ls.	
		125 to 800			Salem Ls.	Sanders
					south Harrodsburg Ls.	
					Muldraugh Fm. | Ramp Creek Fm.	
		3 to 750	— Floyds Knob Ls.		Edwardsville Fm.	Borden
					Spickert Knob Fm.	
					New Providence Sh.	
		90 to 350			*southwest* Rockford Ls. | *northeast* Coldwater Sh.	
359					New Albany Sh. | Sunbury Sh.	
						Ellsworth Sh.

Figure 4. General stratigraphic column for Paleozoic rocks in Indiana. From Thompson and Sowder (2006).
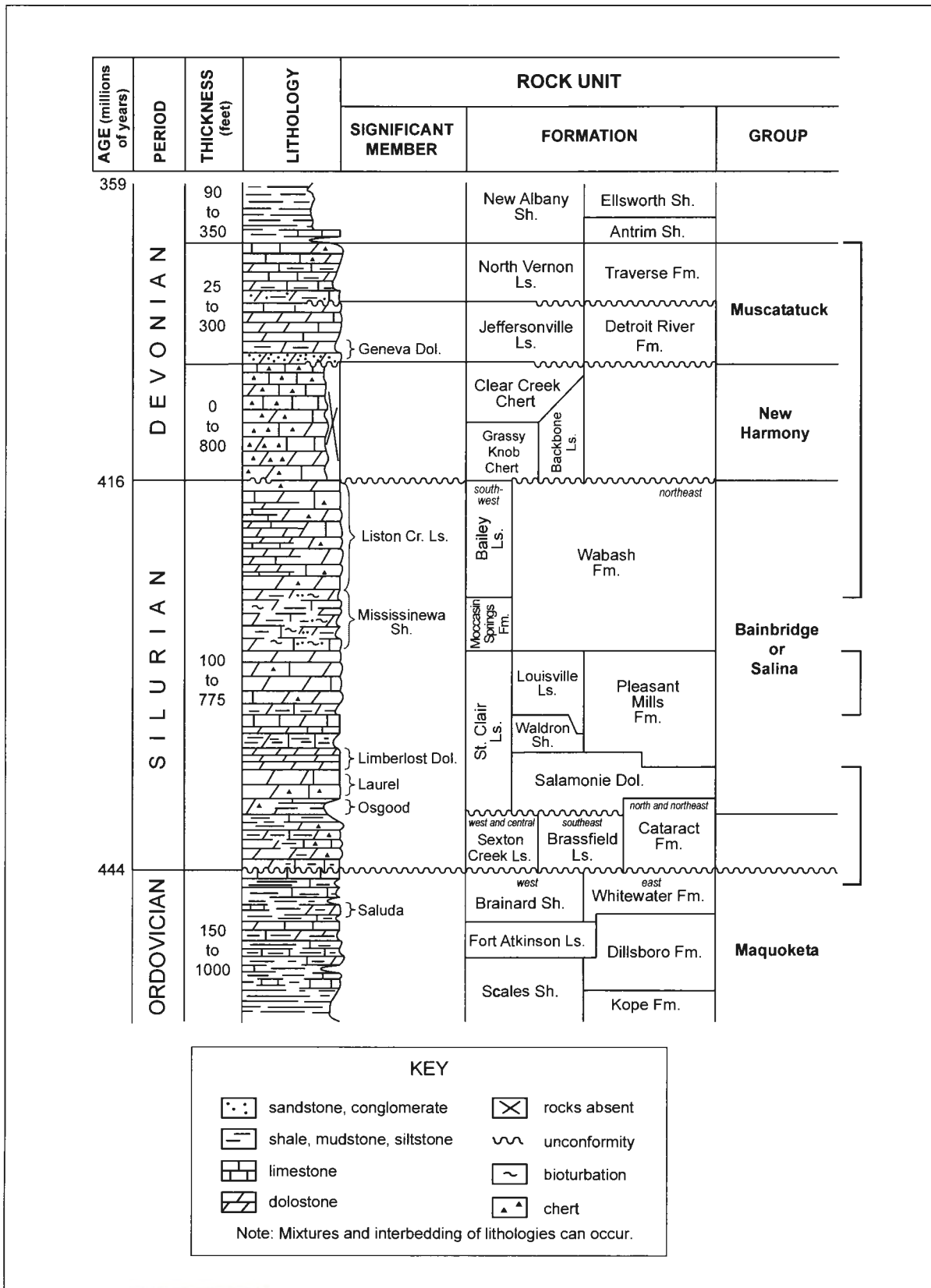
Figure 4 (cont). General stratigraphic column for Paleozoic rocks in Indiana. From Thompson and Sowder (2006).

**COAL-FIRED ELECTRIC
GENERATING STATIONS:**

PRIVATE
1 Indianapolis Power & Light
2 Duke Energy
3 Northern Indiana Public
   Service Co.
4 Indiana-Michigan Power Co.
5 Vectren

COOPERATIVE
6 Hoosier Energy

MUNICIPAL
7 Jasper
8 Logansport
9 Crawfordsville
10 Peru
11 Richmond

OUT-OF-STATE
12 AmerenCIPS (IL)
13 Dominion Energy (IL)
14 Louisville Gas & Electric
    Co. (KY)
15 Kentucky Utilities (KY)
16 Owensboro Municipal
    Utilities (KY)
17 Big Rivers (KY)
18 Duke Energy (OH)
19 Indiana-Kentucky Electric
    Corp. (OH)

UNIVERSITY
20 Purdue
21 Notre Dame

EXPLANATION
● Crushed stone quarry
◎ Ground limestone
◯ Underground crushed
   stone quarry
◆ Lime plant

Coal-fired electric plants
■ Unscrubbed
■ Scrubbed with limestone*
● Scrubbed with lime*
◆ Planned limestone scrubbers*
* 1 or more units

Source of Limestone Used for
Pollution Control and Tons
—— <100,000
—— 100,000–199,000
—— 200,000–299,000
—— >300,000

Figure 5. Map of Indiana showing locations of stone quarries and coal-fired electric-generating stations in and near Indiana. Modified from Ault (1993b).

and Sanders Groups are mined. Another quarry belt defines an arc from New Albany through Indianapolis and into Hamilton County. This group of quarries exploits mainly Devonian rocks, some Silurian rocks, and even a small amount of Ordovician rocks, in Decatur, Franklin, Ripley, and Rush Counties (fig. 3). These follow along the Cincinnati Arch. A separate grouping of quarries from Wayne County to Allen County trends diagonally to Lake County and constitutes part of a series of quarries that ring the Michigan Basin. These quarries produce mainly Silurian rocks and smaller amounts of Devonian formation rocks. Most of these quarries are dominated by dolomite. Quarries in this area are far removed from generating stations, so few quarries from this area were sampled. A map showing locations of existing quarries appears as Figure 5 (after Ault, 1993b). This map also shows locations of coal-fired electric-generating stations. Many stations are located in southwestern Indiana near Indiana's coal fields. Current sources of scrubber stone are noted on the map.

Sampling and Preparing

Thirty-two of the 95 quarries were sampled (Table 2; fig. 6). In most, samples were taken from the active face on the basis of gross lithology (megascopic rock characteristics). In three cases (Gosport, Putnamville, Cape Sandy) rock cores were substituted for face samples owing to logistical problems. Two samples were obtained from the Indiana Department of Transportation. Descriptions of samples are in Appendix A of Shaffer and Sadowski (2000). Figure 7 shows details of sampling for an individual quarry. Individual samples were composited, on the basis of unit thicknesses, into a single sample for each bench. Benches range from a few feet to more than 100 feet in thickness and they constitute the different levels that are quarried as mine units. Each mined unit usually contains a number of lithologically distinct beds (fig. 7).

Samples were washed, then crushed in a chipmunk jaw crusher to a mean diameter of about 0.25 inch. Samples were split by cone and quarter methods and one part further crushed to less than 200 mesh (0.0029 in., 75 μm) for reactivity, chemical, and mineral analyses. One coarse fraction was used for physical property and grindability determinations and one fraction was retained as an archive sample.

ANALYTICAL METHODS

Physical properties

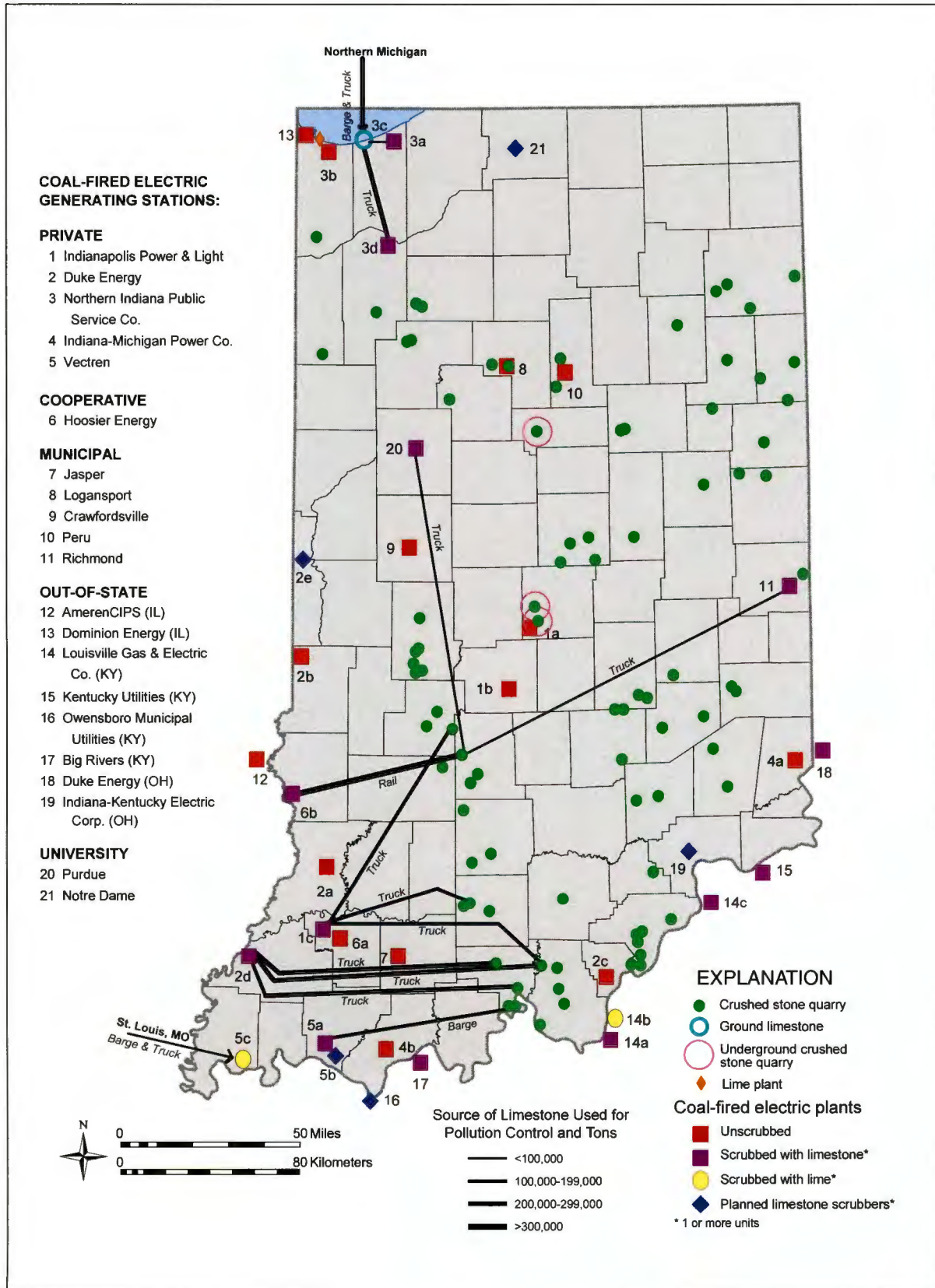The physical properties of rocks determine how easily they can be mined and processed. Data for specific gravity (weight of rock relative to an equal volume of water) and absorption (rough measure of pore space) were determined by immersing specimens in water and comparing dry and wet weights in procedures outlined in Appendix B of Shaffer and Sadowski (2000).

Grindability measures the amount of energy needed to reduce stone to particle sizes useful in wet scrubbing. The exact procedure is a modification of ASTM method D408 as detailed in Appendix B of Shaffer and Sadowski (2000). A specific weight of stone is ground in a small ball mill (fig. 8) and the number of revolutions counted for specific time intervals. Plots of percentages of stone passing a 200-mesh sieve are plotted against revolutions (fig. 9) to determine grindability. Hard stones have lower values than softer, more easily ground stones.

Chemical analyses

The noncarbonate portion of stone is not useful in removing SO_2. This acid-insoluble material was separated by dissolving the entire carbonate portion in weak hydrochloric acid, then washing, filtering, and weighing the remaining nonreactive materials. Insoluble residues are reported as weight percent. The mineralogy of samples was determined by standard X-ray diffraction methods as were mineralogies of insoluble residues. X-ray techniques are noted in Appendix B of Shaffer and Sadowski (2000). Selected samples were dissolved for chemical analyses by methods detailed in Appendix B of Shaffer and Sadowski (2000) and analyzed by emission spectrography.

Reactivity analyses

Fifty samples were analyzed in a lab-scale reactor (fig. 10) to determine their dissolution rates or reactivities. Details of the procedure are given in Appendix B of Shaffer and Sadowski (2000). Stone samples were slurried and reacted under controlled temperature and pH conditions in the reaction vessel. At specific time intervals the slurry was sampled and amounts of dissolved calcium
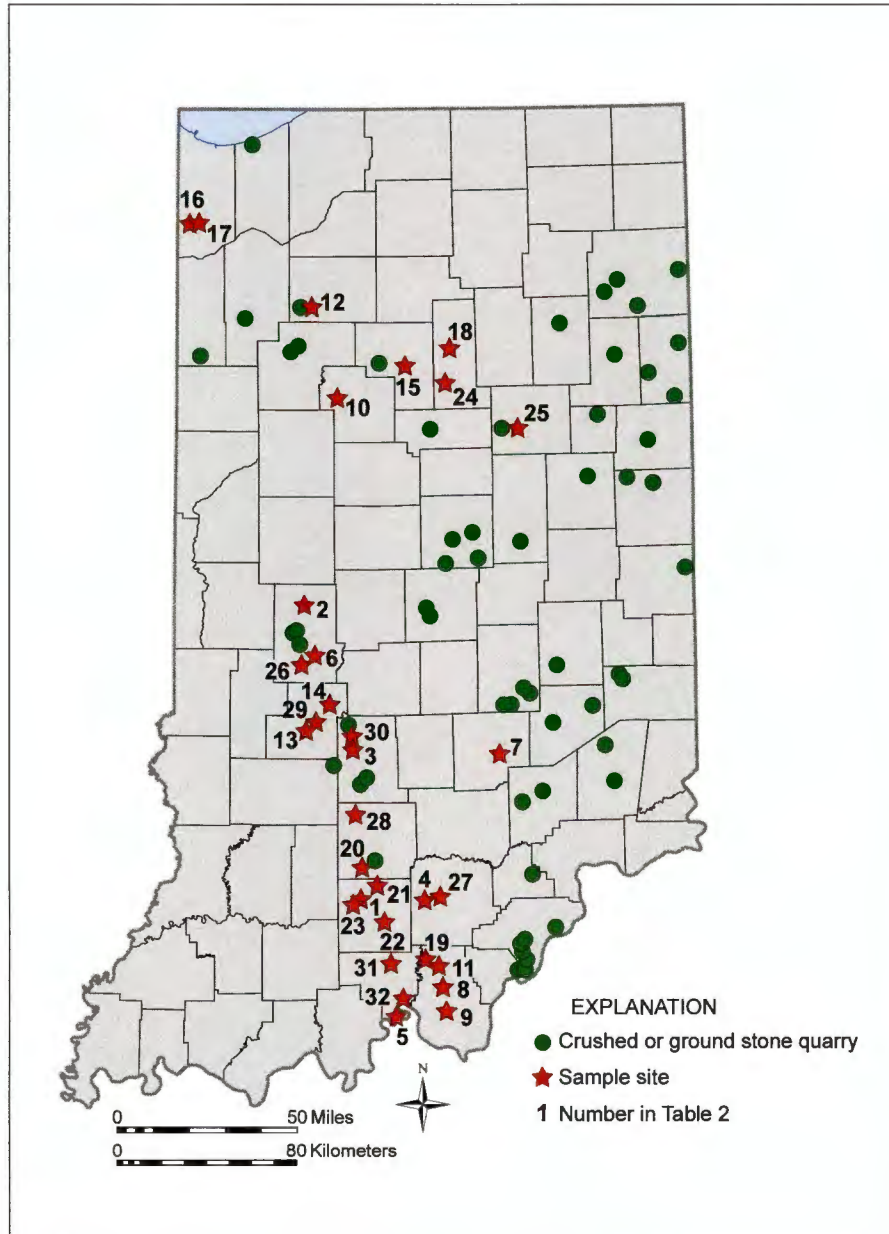
Figure 6. Map of Indiana showing location of quarries and scrubber stone sampled. From Shaffer and Sadowski (2000).

Table 2. Locations of sampled limestones for potential scrubber stones

Site no.	Quarry	Operator	County	Location				Rock unit
				Quarter	Sec.	T.	R.	
1	Abydel	Mulzer Crushed Stone	Orange	NW	28	2 N.	1 W.	Ste. Genevieve Limestone Formation
2	Bainbridge	Harris Stone Service	Putnam	SE NW	15	15 N.	4 W.	Ste. Genevieve Limestone Formation
3	Bloomington	Rogers Group	Monroe	SE SW	27	9 N.	2 W.	Paoli Limestone Formation, Ste. Genevieve Limestone Formation
4	Campbellsburg	Owsley Limestone	Washington	SW	31	2 N.	3 E.	Ste. Genevieve Limestone Formation
5	Cape Sandy	Mulzer Crushed Stone	Crawford	SE SE	25	4 S.	1 E.	Paoli Limestone Formation, Ste. Genevieve Limestone Formation
6	Cloverdale	Martin Marietta Aggregates	Putnam	NW	25	13 N.	4 W.	Ste. Genevieve Limestone Formation, St. Louis Limestone Formation
7	Columbus	Meshberger Stone	Bartholomew	NW SW	5	8 N.	7 E.	Louisville Limestone Formation
8	Corydon	Corydon Crushed Stone	Harrison	SE	14	3 S.	3 E.	Ste. Genevieve Limestone Formation
9	Corydon	Mathes Stone	Harrison	NE	13	4 S.	3 E.	Ste. Genevieve Limestone Formation
10	Delphi	U.S. Aggregates	Carroll	SW	19	25 N.	2 W.	Wabash Formation
11	DePauw	Davis Crushed Stone	Harrison	SE	14	3 S.	3 E.	Paoli Limestone Formation, Ste. Genevieve Limestone Formation
12	Francesville	Ward Stone Co.	Pulaski	SE	16	29 N.	4 W.	Muscatatuck Group
13	Freedom	American Aggregates	Owen	NE	30	10 N.	3 W.	Ste. Genevieve Limestone Formation
14	Gosport	J. W. Jones	Owen	SW	24	11 N.	3 W.	Salem Limestone Formation
15	Logansport	Engineering Aggregates	Cass	SE	6	26 N.	2 E.	Kokomo Limestone Member
16	Lowell	Lowell Mining	Lake	SE	9	32 N.	9 W.	Traverse Formation
17	Lowell	Northern Indiana Materials	Lake	SW	10	32 N.	9 W.	Traverse Formation, Wabash Formation
18	Mill Creek	Stoneco Inc.	Miami	W	29	26 N.	4 E.	Kokomo Limestone Member
19	Mill Town	Robertson Crushed Stone	Harrison	SE	13	2 S.	3 E.	Paoli Limestone Formation, Ste. Genevieve Limestone Formation
20	Mitchell	Rogers Group	Lawrence	SW	7	3 N.	1 W.	Paoli Limestone Formation, Ste. Genevieve Limestone Formation
21	Orleans	Rogers Group	Orange	NW	25	3 N.	1 W.	Ste. Genevieve Limestone Formation
22	Paoli	Calcar Quarries	Orange	SE	6	1 N.	1 E.	Ste. Genevieve Limestone Formation
23	Paoli	Cave Quarries	Orange	SE	29	2 N.	1 W.	Ste. Genevieve Limestone Formation
24	Peru	Rock Industries	Miami	SW	20	27 N.	4 E.	Mississinewa Shale Member
25	Pipe Creek Jr.	Irving Materials	Grant	N	2	24 N.	6 E.	Wabash Formation
26	Putnamville	Kentucky Stone Co.	Putnam		29	13 N.	4 W.	Ste. Genevieve Limestone Formation
27	Salem	Hoosier Stone	Washington	NW	19	2 N.	4 E.	Salem Limestone Formation
28	Siebolt	Rogers Group	Lawrence	SE	11	6 N.	2 W.	Paoli Limestone Formation, Ste. Genevieve Limestone Formation
29	Spencer	Rogers Group	Owen	NE	19	10 N.	3 W.	Ste. Genevieve Limestone Formation
30	Stinesville	Hoosier Calcium	Monroe	N	20	10 N.	2 W.	Salem Limestone Formation
31	Temple	Mulzer Crushed Stone	Crawford	SE	16	2 S.	1 E.	Paoli Limestone Formation, Ste. Genevieve Limestone Formation
32	Tower	Mulzer Crushed Stone	Crawford	NW	29	3 S.	2 E.	Ste. Genevieve Limestone Formation

Depth (feet)

Limestone. 5% to 10% sand. Oolite skeletal grainstone.

Sandstone. Mud clasts.

Limestone. Pellet mudstone. Some skeletal debris. Stylolites spaced ~8 inches. Brown at top, buff downward.

Limestone. Oolite grainstone. Buff with minor skeletal debris.

Limestone. Oolite echinoid, grainstone.

Limestone. Oolite grainstone with 15% skeletal debris. Buff to cream colored with stylolites spaced 8 inches.

Limestone. Pellet mudstone. Beds 1 to 4 inches thick have ¼-inch green shale partings between. Beds up to 6 inches in lower third.

Sandstone and sandy limestone.

Limestone. Oolite skeletal pellet packstone. Buff, some algae.

Limestone. Algal boundstone.

Limestone. Skeletal pellet grainstone.

Limestone. Silty with few weak stylolites. Silt abundant in basal foot.

Limestone. Cream oolite grainstone. Some brachiopods. Medium grained.

Limestone. Pellet skeletal grainstone 5% sand in basal 10 inches.

Limestone. Sandy brecciated wackestone.

Limestone. About 10% sand concentrated in ¼- to ½-inch laminae spaced 1.5 to 2 inches. Broadly crossbedded. Pellet skeletal grainstone.

Limestone. Skeletal grainstone. Few weak stylolites.

Limestone and chert. Pellet packstone.

Limestone. Skeletal pellet mudstone to packstone with zones gradational into thin silty shales (4 to 8 inch total) spaced evenly through the interval. Top 2 inches finely laminated (tidal?).

Dolostone. Dense, medium gray, pure.

Limestone. Light gray-buff skeletal pellet packstone to mudstone. Stylolites spaced ½ to 6 inches. Thin grainstone at base.

Dolostone and dolomitic limestone. Dolostone top ⅔ is soft and friable. Bottom ⅓ skeletal wackestone.

Chert. Light brown, laminated.

Mixed dolostone, dolomitic limestone, and limestone. Few fossil debris. Characteristic hexacoral zone ¾ through interval. Minor chert.

Limestone and chert.

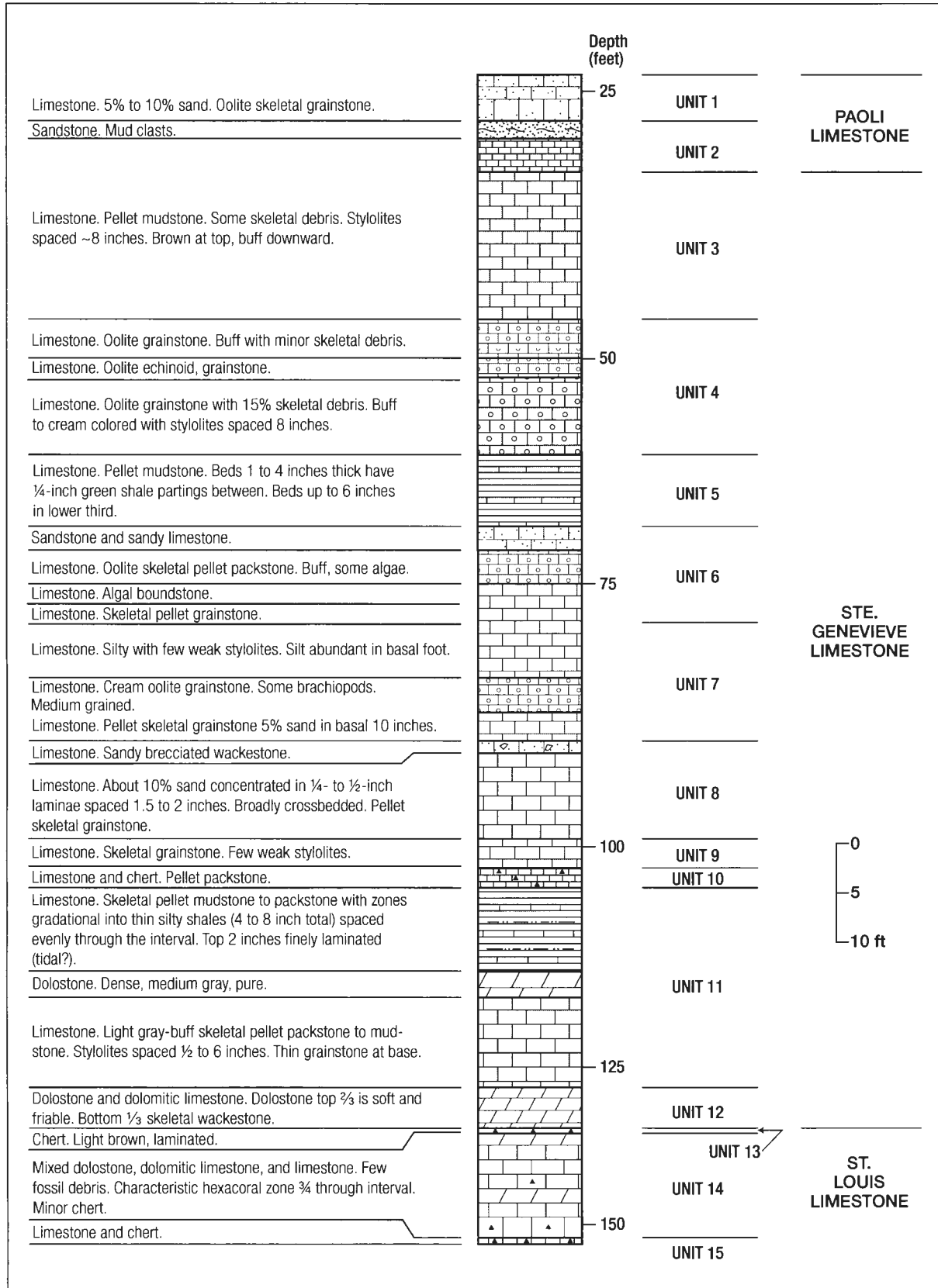| Depth	Unit	Formation
25	UNIT 1	PAOLI LIMESTONE
	UNIT 2	
	UNIT 3	
50	UNIT 4	
	UNIT 5	
75	UNIT 6	STE. GENEVIEVE LIMESTONE
	UNIT 7	
	UNIT 8	
100	UNIT 9	
	UNIT 10	
	UNIT 11	
125	UNIT 12	
	UNIT 13	ST. LOUIS LIMESTONE
	UNIT 14	
150	UNIT 15	

0
5
10 ft

Figure 7. Illustration showing detailed section of part of the Paoli and Ste. Genevieve Limestones in Indiana.

determined by autotitrator to determine reactivity values (fig. 11).

ANALYTICAL RESULTS

Absorption/Specific gravity

Specific gravity determinations (Table 3) range from 2.20 to 2.69 and average 2.57. Generally, lower specific gravity values came from clay-rich rocks (2.20), very porous samples of Salem Limestone (2.21), and certain oolite beds (2.40). Absorption percentages ranged from 0.3 to 10.3 percent with an average of 2.34 percent. Clay-rich rocks tended to have high absorption values (up to 10.3 percent) as do pure rocks from the Salem Limestone (7.7 percent). Dolomites tended to show relatively high absorption of 3 to 4 percent. Oolitic-rich beds also tended to show good absorption of 4 to 5 percent. Fine-grained crystalline limestones showed low absorption, occasionally less than 1 percent.

Grindability

Grindability values range from 7.0 to 21.7. The entire set averages 12.12 (Table 4). The most easily ground stone (values of 7 to 10) came from reefs in northern Indiana and from oolitic beds of the Ste. Genevieve Limestone. Relatively soft stones (10.5) also came from the Salem Limestone. Cherty limestones of the St. Louis Limestone (Mississippian) tended to show higher grindability values (12 to 21) as did some of the limestone reefs. In terms of ease of grinding, oolitic rocks of the Ste. Genevieve Limestone, Salem Limestone, and dolomites of the Wabash Formation rank best.

Insoluble residue

Acid-insoluble residues of bulk samples ranged between 1.1 to 17.2 percent and averaged 5.2 percent for all samples (Table 5). Very high values (up to 55 percent) came from argillaceous or quartz-bearing samples. Silica occurred as small detrital grains or commonly as chert. The St. Louis Limestone was notably rich in chert, having insoluble contents in the 8 to 17 percent range. Residues in pure limestones commonly were in the 1 to 3 percent range.

Mineralogy

In addition to visual examination, samples were analyzed by X-ray diffraction to determine mineralogy of samples. An example of a diffractogram (fig. 12) shows the dominant mineral is calcite. Dolomite is seen in a number of samples. Table 6 summarizes mineralogy with percentages given in Table 7. Variations in lithology are noted in Figure 7, a detailed section of one quarry.

Other major minerals are quartz, clays (mainly illite), pyrite, and hematite. Clays occur dispersed in carbonate matrix; as thin laminae; and as distinct thin beds, stylolites, and fillings of dissolution features. Quartz occurs primarily as chert that forms thin beds or nodules as rounded grains of detrital material and fillings of dissolution features. Pyrite and other sulfide minerals occur as crystals in carbonate matrix.

Hematite occurs primarily as cementing material or as coatings on weathered surfaces. Pyrolusite occurs primarily as coatings.

A number of trace minerals were noted mainly as late-formed cavity fillings. While distinctive, they are volumetrically unimportant. Organic material was prominent in thin dark-brown to black laminae or as stylolites. Organics are not minerals in the strictest sense but they can be significant components. Calcite and dolomite occur in a number of different forms as summarized in Table 8. Coarse single crystals of calcite known as spar is a common cement, but may also make up to 97 percent of the rock and averages 22 percent. Recognizable fossil fragments average 23 percent. Large grains formed by wave action, such as ooids, and by organic processes, including pellets, average 8.2 percent and 9.7 percent, respectively. Very fine grained micrite is the dominant type averaging 34.8 percent. Intraclasts or pebbles of preexisting carbonates were relatively rare at about 3 percent.

Chemical analyses

Chemical analyses are reported in Table 9. The purest carbonates contained more than 98 percent calcite. Values for the entire set of samples ranged from 48 to 98.2 percent calcite and averaged 81.8 percent. Dolomites and mixed limestone/dolomite

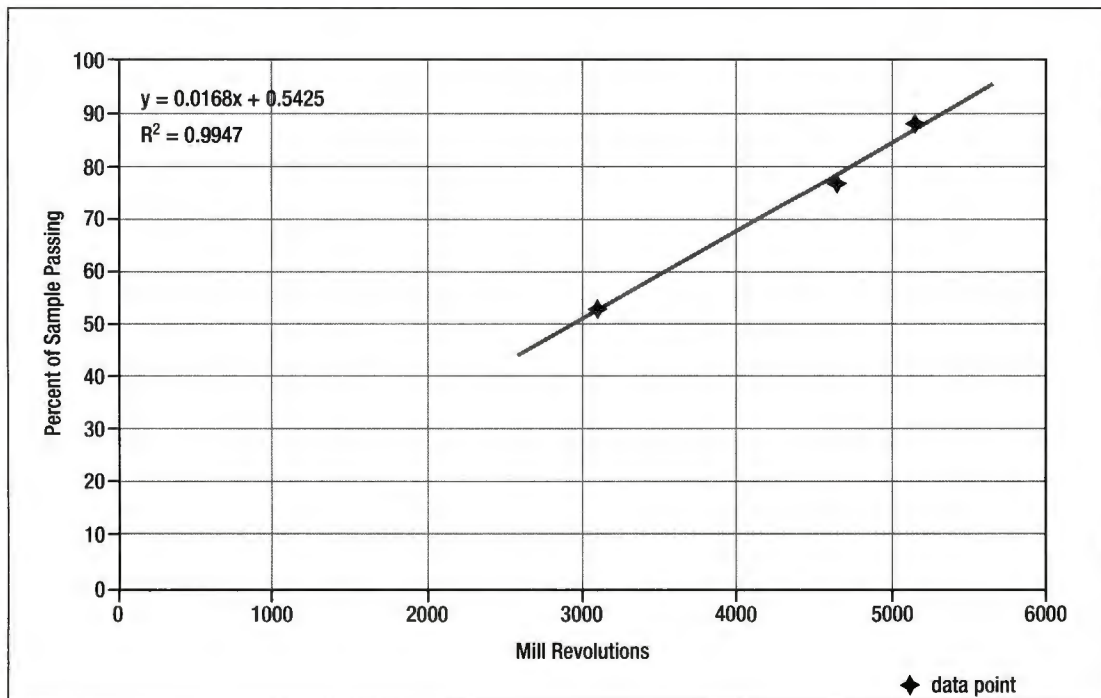Figure 8. Photograph of device for determining grindability of stone samples.

Figure 9. Graph used to determine grindability of scrubber stone samples.

Figure 10. Photograph of device for determining reaction rates of stone samples.
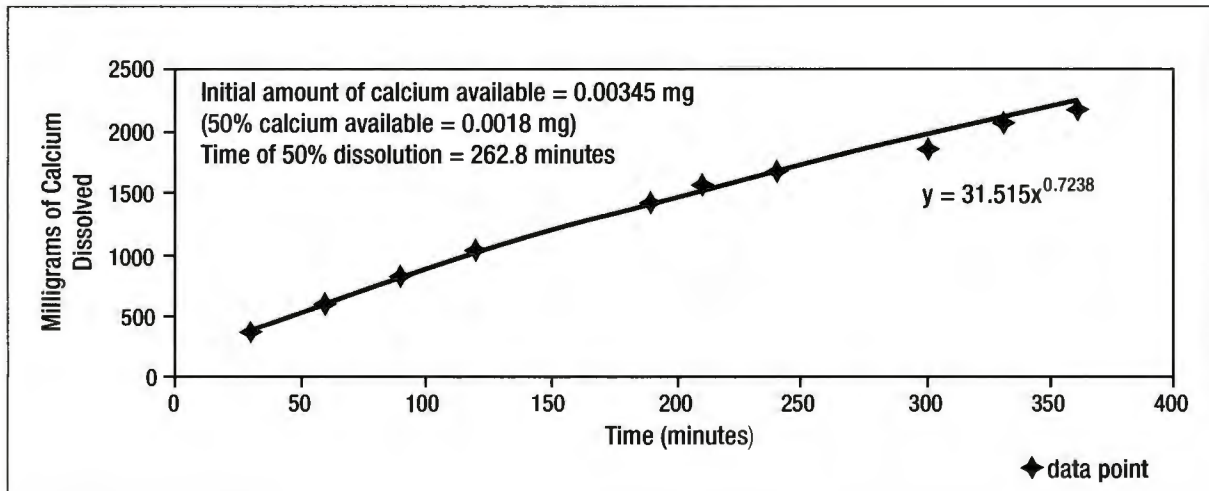

Figure 11. Graph showing derivation of dissolution rate or reactivity of limestone samples.

Table 3. The physical properties of scrubber stone arranged stratigraphically by quarry

Site	Bench	Unit	Specific gravity	Absorption (%)
Abydel		19	2.58	1.9
	II	-	-	-
		18	2.62	1.9
		17	2.63	1.9
		16	-	-
		15	2.56	2.7
		14	2.47	4.3
		13	2.55	2.4
		12	2.60	1.7
		11	2.59	1.7
		10	2.56	2.6
		9	2.54	2.4
	I	8	2.60	1.6
		7	2.63	1.5
		6	2.20	10.3
		5	2.50	1.8
		4	2.45	4.3
		3	2.54	2.4
		2	2.63	1.3
		1	2.61	1.6
Bainbridge		4	2.63	3.2
		3	2.60	1.9
		2	2.61	1.7
		1	2.53	3.1
		0	2.48	4.6
Bloomington	II	-	-	-
	I	-	-	-
		11	2.65	0.8
		10–4	-	-
		3	2.66	0.7
		1–2	-	-
Cape Sandy			2.62	1.5

Site	Bench	Unit	Specific gravity	Absorption (%)
Cloverdale	II	(A-G)	2.54	2.0
		A	2.58	2.1
		B	2.58	2.1
		C	2.56	2.6
		D	2.59	2.0
		E	2.60	1.8
		F	2.24	1.5
		G	2.60	1.8
	I	(H-L)	2.60	1.8
		H	2.60	2.3
		I	2.61	1.6
		J	2.61	1.7
		K	2.61	1.4
		L	2.56	2.2
Corydon	III		-	-
	II		-	-
	I		2.63	1.1
Francesville			2.69	1.1
Logansport			2.69	0.3
Lowell Mining		3	2.62	3.3
		2	2.61	2.8
		1	2.54	4.1
Lowell Reef	III	A	2.60	2.7
		B	2.58	3.0
	II	C	2.69	2.9
		B	2.67	1.8
		A	2.68	1.7
	I	C	2.63	2.2
		B	2.63	2.4
		A	2.67	1.9
Mill Creek	III		2.57	2.4
	II		-	-
	I		2.44	4.3
Mill Town	IV	1	2.66	0.7
	III	2	2.55	2.2
	II	3+4	2.57	1.7
	I	5+6	2.60	1.3
Mitchell		A	2.66	0.9, 0.7
		B	2.60	1.5

Table 3 (cont.) The physical properties of scrubber stone arranged stratigraphically by quarry

Site	Bench	Unit	Specific gravity	Absorption (%)
		A	2.62,2.65	1.3, 1.2, 1.1
Orleans		X	2.44	3.9
		Y	2.40	4.7
Peru			2.34	6.2
Pipe Creek Jr.		1	2.64	0.8
		4	2.43	5.2
		3	2.45	3.9
Putnamville		2	2.63	1.3
		1	2.63	1.1
		11	2.61	10.4
		10	2.58	2.3
		9	2.60	1.7
		8	2.58	2.1
		7	2.64	1.8
Sieboldt		6	2.57	2.1
		5	2.56	2.4
		4	2.62	2.2
		3	2.60	2.1
		2	2.59	3.2
		1	2.54	2.7
		6	2.58	2.2
		5	2.55	2.5
		4	2.57	2.0
Spencer		3	2.49	3.4
		2	2.57	2.2
		1	2.61	1.5
Stinesville			2.21	7.7
	V	8	2.63	1.6
	IV	6	2.65	1.0
		5	2.65	2.64
Temple			1.4	0.9
	III	4	-	-
	II	2	2.67	0.6
	I	1	2.47	2.8
	III		2.60	1.8
	II		2.51	2.9
Tower	I		-	-
	grab		2.61	1.5

Table 4. Scrubber stone grindability index

Composite	Grindability index
Abydel Bench I	11.79
Bainbridge Unit 4	13.33
Bainbridge Unit 3	11.49
Bainbridge Unit 0	21.74
Bloomington Bench II	11.67, 11.63
Bloomington Bench I	12.20
Cloverdale Bench II	16.53
Cloverdale Bench I	12.90
Columbus	13.78
Delphi Bench I	10.02
Francesville	10.81
Gosport	16.42
Lowell Mining	9.30
Lowell Bench III	12.90
Lowell Bench II	8.62
Lowell Bench I	8.16
Mill Town Bench III	18.18
Mill Town Bench II	11.57
Mill Town Bench I	10.87
Mitchell	12.45
Orleans Unit A	12.93
Orleans Unit X	7.25, 7.84, 7.46
Pipe Creek Jr. East	17.27
Pipe Creek Jr. West	16.69
Putnamville Unit 3	12.90
Putnamville Unit 2	16.67
Spencer	12.66, 11.81
Spencer (Scrubber Pile)	7.76
Stinesville	10.57
Temple Unit 7	17.24
Temple Unit 6	13.16, 12.92
Temple Bench Unit 5	10.99, 10.99
Temple Bench III	13.79, 14.81
Temple Bench II	8.51
Temple Bench I Unit 2	7.04
Temple Bench I Unit 1	10.05, 10.00
Tower Bench III	10.26, 11.76
Tower Bench II	13.16
Tower Bench I	16.13

samples came from the Wabash Formation, the Kokomo Limestone Member of the Wabash Formation (Silurian), the Traverse Formation (Devonian), and the Ste. Genevieve Limestone units. If these dolomitic-bearing samples are omitted, the average for calcite is 86.5 percent.

Dolomite, which is known to reduce efficiency of sorption, ranged from 0.2 to 46.9 percent and averaged 10.3 percent. Most samples were relatively low in dolomite, but 25 samples did exceed 10 percent. Most dolomite samples were from the Wabash Formation in reefs of northern Indiana, but dolomite-rich beds also occurred in the St. Louis Limestone and some in the Ste. Genevieve Limestone.

Silica (SiO_2) values ranged from 0.2 to 38 percent and averaged 8.56 percent. Two samples were very rich in quartz with an average of 33.2 percent. Omitting those two samples results in an overall average silica content of 8.0 percent. Silica is present as quartz and clay minerals that also include alumina. Alumina (Al_2O_3) values positively correspond in most cases with silica concentrations. It ranged from 0.05 to 0.28 percent and averaged 0.93 percent and is present primarily as clay minerals. A thin clay-rich, and hence alumina-rich, unit at the base of the Paoli Limestone was the only clay-rich unit noted.

Iron as Fe_2O_3 ranged from 0.08 to 2.69 percent and averaged 0.54 percent. Iron can occur as pyrite (FeS_2) which reduces stone sorption efficiency. Titanium (TiO_2) and manganese (MnO) were generally very low, with most MnO occurring in weathered zones as black coatings of pyrolusite. Strontium (Sr) was also present in low amounts.

Limestone reactivity with SO_2

Data for reactivity expressed as dissolution rate are reported in Table 10 as are Ca/Mg ratios of reacted fluids. Ca/Mg ratios vary from 1.01 to 94.09. Dissolution rates varied from 9.99×10^{-5} to 1.20×10^{-3}. The most reactive stones came from Ste. Genevieve Limestone samples. Wabash Formation dolomites were the slowest by a factor of 10. Rocks from the Louisville Limestone, St. Louis Limestone, and Traverse Formation were also relatively low in reactivity.

The PRISM computer model is based upon chemical engineering principles. It models real-world

Table 5. Scrubber stone insoluble residue values

Site	Bench	Unit	% Insoluble residue
Abydel		19	1.1
		18	1.3
		17	2.8
	II	16	-
		15	45.0
		14	8.1
		13	8.7
		12	1.6
		11	3.8
		10	21.5
		9	55.1
		8	2.5
		7	4.3
		6	23.3
	I	5	3.9
		4	-
		3	1.5
		2	1.1
		1	2.6
Bloomington	II		10.8
	I		3.9
		1-11	-
Bainbridge		4	8.6 , 7.9
		3	10.4
		2	17.2
		1	13.7
		0	12.9
Cape Sandy			2.7

Table 5 (cont.). Scrubber stone insoluble residue values

Site	Bench	Unit	% Insoluble residue
Cloverdale	II	(A-G)	2.3
		A	3.1
		B	4.6
		C	1.6
		D	2.6
		E	3.7
		F	2.8
		G	6.8
	I	(H-L)	5.2
		H	1.7
		I	3.0
		J	4.0
		K	8.8
		L	12.2
Columbus			3.6
Corydon		4	-
		3	-
		2	-
		1	6.3
Francesville			6.1
Logansport			9.5
Lowell Mining		3	4.2
		2	13.6
		1	4.7
Lowell Reef	III	3	2.2, 2.1
	II	2	0.4
	I	1	3.8
Mill Creek	III	1	0.3
	II	2	-
	I	3	12.2
Mill Town	IV	1	2.5
	III	2	3.1
	II	3+4	3.6
	I	5+6	3.9, 3.6
Mitchell		A	6.9
		B	2.5

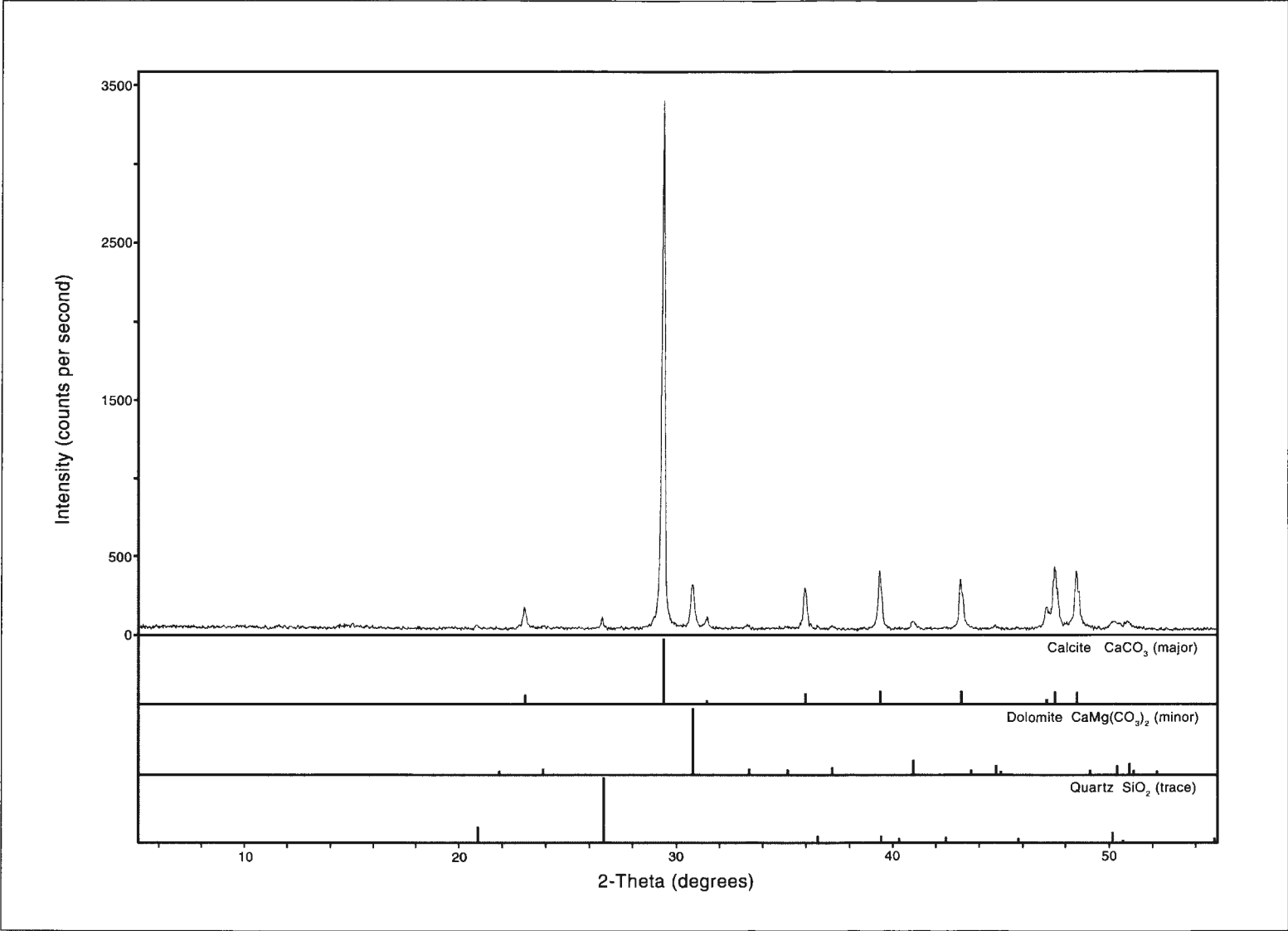| Site	Bench	Unit	% Insoluble residue
Orleans		3	2.5 , 2.4, 2.2
		2	1.2 , 1.0
		1	0.7 , 0.9
Peru			45.7
Pipe Creek Jr.		2	-
		1	1.9
Putnamville		4	-
		3	3.3
		2	2.6
		1	0.4
Sieboldt		11	2.8
		10	4.0
		9	8.3
		8	7.0
		7	2.0
		6	10.6
		5	4.7
		4	2.3
		3	4.9
		2	5.0
		1	2.4
Spencer		6	6.5
		5	5.5
		4	12.9
		3	5.5
		2	6.2
		1	6.7
Stinesville			2.2
Temple	V	8	5.0
	V	7	3.1
	IV	6	2.6
	III	5	-
		4	-
	II	2	8.5
	I	1	2.9
Tower	III		8.3
	II		11.8
	I		-
	grab		22.6

Figure 12. X-ray diffractogram of scrubber stone samples from Corydon Quarry, Harrison County. The samples contain calcite plus minor dolomite and quartz.

Table 6. Mineralogy of scrubber stone samples

Major minerals			
Calcite $CaCO_3$		Dolomite $CaMg(CO_3)_2$	
Common minerals			
Clay (illite) $K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$	Quartz SiO_2	Pyrite FeS_2	Hematite Fe_2O_3
Trace minerals			
Pyrolusite MnO	Fluorite CaF_2	Gypsum $CaSO_4 \bullet 2H_2O$	Sphalerite ZnS
Celestite $SrSO_4$	Organics		

Table 7. Petrologic data for scrubber stone samples (in percent)

Component	Range	Average	Standard deviation
Calcite	1–98	6.0	9.7
Dolomite	0.3–100	26.8	28.5
Quartz	0–23.7	2.6	4.4
Clay	0–6.3	2.1	2.3
Pyrite	0–20.0	1.2	2.9
Miscellaneous	0–8.3	1.0	1.3
Porosity	1–21	2.4	3.5

Table 8. Carbonate components of thin sections (in percent)

Component	Range	Average
Spar/Cement	0.3–97	22.5
Ooids	0.3–46.9	8.2
Pellets	0.2–38.0	9.7
Fossils	0.3–76.8	23.2
Micrite	0.2–98.8	34.8

Table 9. Chemical analyses of scrubber stone samples

Sample	CaO	CaCO$_3$	MgO	MgCO$_3$	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	MnO	SrO	Total
Abydel Bench II	48.7	86.9	1.9	4.0	7.44	0.80	0.42	0.05	0.01	0.05	99.67
Abydel Bench I	44.8	80.0	4.9	10.4	7.45	0.99	1.04	0.06	0.04	0.05	100.01
Bainbridge Unit 0	29.3	52.3	19.1	39.9	6.38	0.80	1.11	0.03	0.06	0.01	100.59
Bainbridge Unit 1-3	48.7	87.0	0.4	0.8	11.0	0.65	0.41	0.04	0.03	0.03	99.97
Bainbridge Unit 1-4	52.3	93.3	0.5	1.1	4.01	0.63	0.43	0.03	<.01	0.02	99.53
Bainbridge Unit 4	53.8	96.0	0.6	1.2	1.68	0.50	0.41	0.02	0.01	0.04	99.86
Bloomington Bench II	52.8	94.2	0.5	1.0	4.46	0.51	0.18	0.02	0.01	0.04	100.42
Bloomington Bench I	53.5	95.4	0.1	0.2	3.65	0.36	0.25	0.02	0.05	0.05	99.98
Campbellsburg	51.5	91.9	1.0	2.0	4.66	1.10	0.69	0.05	0.03	0.03	100.46
Cape Sandy-Paoli	47.8	85.3	2.6	5.5	7.03	1.33	0.63	0.08	0.03	0.08	99.98
Cape Sandy-Ste. Genevieve	49.2	87.8	3.3	6.8	4.46	0.83	0.31	0.04	0.01	0.06	100.31
Cave Stone Paoli Bench IV	50.5	90.1	3.0	6.3	2.93	0.66	0.26	0.03	0.02	0.04	100.27
Cave Stone Paoli Bench III	47.0	83.9	1.7	3.6	10.2	1.54	0.70	0.07	0.03	0.06	100.12
Cave Stone Paoli Bench II	47.1	84.1	1.5	3.2	10.6	1.56	0.63	0.10	0.03	0.06	100.28
Cave Stone Paoli Bench I	31.8	56.7	1.7	3.5	28.30	8.92	2.27	0.38	0.05	0.03	100.15
Cloverdale Composite	53.2	94.9	0.8	1.7	2.54	0.54	0.53	0.03	0.03	0.03	100.30
Cloverdale Bench II	53.2	95.0	0.6	1.2	2.54	0.48	0.54	0.03	0.00	0.04	99.83
Cloverdale Bench I	52.4	93.6	0.4	0.9	5.08	0.72	0.32	0.04	0.02	0.04	100.72
Cloverdale Bench	52.1	93.0	0.5	1.0	5.85	0.53	0.28	0.03	0.01	0.04	100.73
Columbus (Louisville)	35.6	63.5	15.3	32.0	3.33	0.56	0.51	0.03	0.01	0.02	99.97
Corydon	45.6	81.4	5.0	10.4	6.47	1.29	0.43	0.05	0.01	0.05	100.10
Corydon	45.1	80.5	5.2	10.8	7.90	0.66	0.23	0.04	0.01	0.04	100.18
Corydon	47.5	84.8	5.3	11.1	3.70	0.55	0.17	0.03	0.01	0.05	100.41
Corydon Bench V	48.0	85.7	5.8	12.2	1.58	0.42	0.17	0.02	0.01	0.04	100.14
Corydon Stone Bench VI	41.0	73.1	10.4	21.7	4.51	0.38	0.19	0.02	0.01	0.02	99.93
Corydon Stone Bench III	37.1	66.2	9.7	20.3	11.2	1.59	0.55	0.08	0.01	0.04	99.97
Corydon Stone Bench II	51.5	92.0	2.2	4.7	2.82	0.39	0.11	0.02	0.01	0.05	100.10
Corydon Stone Bench I	48.5	86.5	2.8	5.9	6.41	1.02	0.30	0.05	0.01	0.05	100.24
DePauw Bench V	50.3	89.8	2.6	5.4	4.82	0.27	0.09	0.02	0.01	0.05	100.46
DePauw Bench IV	47.6	85.0	4.6	9.7	3.42	0.62	0.28	0.03	0.02	0.04	99.11
DePauw Bench III	49.5	88.3	2.6	5.4	5.09	1.05	0.36	0.05	0.02	0.06	100.33
DePauw Bench II	50.5	90.2	1.0	2.0	6.15	1.47	0.50	0.07	0.03	0.05	100.43
DePauw Bench I	26.8	47.9	1.1	2.3	38.0	9.28	2.69	0.49	0.04	0.03	100.68
Delphi Bench II	29.8	53.1	20.6	43.1	2.97	0.35	0.40	0.01	0.05	0.01	99.99
Francesville	30.5	54.5	18.9	39.5	4.40	0.61	1.01	0.03	0.02	0.01	100.08
Freedom	47.8	85.3	2.1	4.3	8.67	1.10	0.44	0.05	0.02	0.03	99.89
Hoosier Calcium	54.6	97.4	0.7	1.4	1.16	0.15	0.11	0.01	0.00	0.03	100.27

Table 9 (cont.). Chemical analyses of scrubber stone samples

Sample	CaO	CaCO$_3$	MgO	MgCO$_3$	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	MnO	SrO	Total
Lowell Mining	28.6	51.1	19.1	39.9	7.30	0.32	2.00	0.02	0.01	0.01	100.66
Lowell Reef Bench III	29.5	52.7	20.7	43.3	2.54	0.47	0.95	<.01	0.02	0.01	99.99
Lowell Reef Bench II	28.9	51.6	20.9	43.7	3.61	1.07	0.54	0.04	0.03	0.01	100.60
Lowell Reef Bench I	30.4	54.2	22.0	46.0	0.24	0.15	0.24	<.01	0.02	0.01	100.87
Lowell Reef Total Composite	29.4	52.5	22.4	46.9	0.22	0.08	0.21	<.01	0.02	0.01	99.90
Mitchell Unit A	48.2	86.1	1.9	4.0	7.63	1.55	0.61	0.07	0.04	0.06	100.06
Mitchell Unit B	50.0	89.3	3.4	7.2	3.08	0.49	0.20	0.02	0.01	0.05	100.35
Orleans Unit X	54.8	97.8	0.6	1.3	0.31	0.19	0.19	0.01	0.01	0.04	99.85
Orleans Unit Y	53.3	95.1	0.6	1.3	2.07	0.43	0.32	0.03	0.01	0.05	99.31
Orleans (A)	55.0	98.2	0.6	1.3	0.26	0.17	0.09	<.01	<.01	0.01	100.05
Pipe Creek Jr. Bench I	53.6	95.7	0.6	1.3	2.15	0.97	0.55	0.05	0.01	0.02	100.75
Putnamville Core Unit 1	53.7	95.8	0.6	1.2	2.30	0.58	0.27	0.04	0.02	0.03	100.24
Putnamville Core Unit 3	37.8	67.5	10.3	21.5	8.85	1.48	0.62	0.09	0.02	0.03	100.09
Mill Town 1	54.0	96.4	0.8	1.7	1.26	0.41	0.20	0.02	0.02	0.07	100.08
Mill Town 2	54.3	96.9	1.0	2.1	1.42	0.25	0.15	0.02	0.01	0.05	100.90
Mill Town Bench IV	45.8	81.7	6.7	14.1	3.51	0.63	0.25	0.03	0.01	0.05	100.28
Mill Town Bench III-IV	45.2	80.7	7.8	16.3	2.16	0.41	0.35	0.02	0.01	0.04	99.99
Mill Town Bench II	54.5	97.2	0.5	1.1	1.23	0.22	0.16	0.01	0.01	0.04	99.97
Mill Town Bench I	54.2	96.8	1.1	2.2	1.17	0.35	0.15	0.01	0.02	0.06	100.76
Spencer	50.8	90.6	1.9	3.9	4.66	0.56	0.21	0.03	0.03	0.03	99.97
Spencer (Scrubber Pile)	48.3	86.2	2.9	6.1	6.87	0.62	0.28	0.03	0.01	0.03	100.14
Stinesville	54.8	97.7	0.6	1.3	1.12	0.05	0.08	0.01	0.02	0.03	100.35
Stinesville	38.8	69.2	6.5	13.6	14.2	1.59	1.53	0.08	0.03	0.03	100.28
Stinesville Bench I	50.5	90.1	3.3	6.9	2.25	0.39	0.24	0.02	0.01	0.04	99.95
Temple 4A	47.6	84.9	4.9	10.2	3.47	1.27	0.92	0.07	0.03	0.10	100.96
Temple 6-G	47.1	84.1	5.5	11.5	2.53	0.62	2.00	0.03	0.11	0.05	100.94
Temple 6-G	48.1	85.9	4.5	9.4	2.10	0.49	1.64	0.03	0.06	0.06	99.68
Temple B	46.2	82.5	2.2	4.5	11.4	1.19	0.51	0.11	0.01	0.06	100.28
Temple Base A	51.8	92.4	2.9	6.1	1.20	0.20	0.08	0.01	<.01	0.04	100.04
Temple Beech Creek 8-H	50.8	90.7	1.7	3.6	3.66	0.94	0.88	0.05	0.06	0.07	99.96
Temple Paoli 4-B	53.3	95.1	1.7	3.6	0.88	0.32	0.51	0.02	0.02	0.06	100.51
Temple Unit B	46.6	83.1	4.3	9.0	7.14	0.85	0.46	0.05	0.01	0.06	100.67
Temple "A"	53.2	94.9	1.9	4.0	1.49	0.14	0.09	0.01	0.01	0.04	100.68
Tower Bench II	45.9	81.9	5.1	10.6	6.83	0.89	0.58	0.05	0.01	0.05	100.91
Tower Bench III	47.7	85.1	3.1	6.5	6.65	1.2	0.62	0.06	0.01	0.08	100.22
Tower Bench III	45.7	81.5	5.0	10.5	5.60	1.18	1.12	0.03	0.02	0.06	100.01
Tower Bench 0	41.3	73.7	7.3	15.2	9.71	0.91	0.28	0.05	0.01	0.01	99.87

FGD wet-scrubbing systems performances using thermodynamic principles and mass balance calculations. The model is licensed to EPRI members and can be tailored for specific units based on operating conditions of that system. The program operated on a model based upon details of Unit 3 of their Petersburg generating station. Andy Scott, Indianapolis Power & Light Company, input data generated by this study into the PRISM model. According to Andy Scott, the simulation operates in an iterative mode and, if samples are not sufficiently pure, the model does not converge to a reportable set of values. Dolomite samples were deemed unacceptable for the parameters of the model.

Data for 50 samples were entered into the PRISM modeling program; results are noted in Table 11. Less than half (22) of the samples produced usable results. Detailed data from model iterations are available in Appendix D of Shaffer and Sadowski (2000). Removal of SO_2 ranged from 88 to 98.3 percent and averaged 90.9 percent. Use of reagent ranged from 1.070 to 1.365×10^4 pounds per minute with an average of 1.077. Utilization of limestone reagent as measured by Si/Ca ratios ranged from 91.2 to 93.5 percent with an average of 92.6 percent. Beds of the Ste. Genevieve Limestone were very effective sulfur sorbents, with most removing 90 percent of the SO_2 and one exceeding 98 percent removal. Salem Limestone also worked well with removal rates exceeding 94 percent and utilization of almost 93 percent.

SCALE FORMATION

The precipitation of solid mineral phases from the calcium sulfite-rich liquors can present problems in FGD. Mineral precipitates can impair efficiencies or even completely block spray nozzles, pipes, and filter media. Blockages can result in expensive repairs and reduced SO_x-removal efficiency, and occasionally require taking FGD units offline for removal of scale. Exact causes of scaling remain unknown. It is likely possible that insoluble minerals, especially clay minerals in the raw material, promote crystallization. Clays are very fine grained in size and relatively reactive owing to unsatisfied surface changes. The most common acid-insoluble mineral is quartz. It is hard and can cause problems related to abrasion.

Figure 13A shows an example of scale formed inside a pipe at an active FGD operation. These patches can grow to appreciable sizes. Crystals are mostly Ca-sulfite and gypsum, although other phases containing metals from the system or traces of mercury and other volatile pollutants can occur. Minerals form as fibers (fig. 13B) in subparallel growth patterns that combine to show external botryoidal surfaces (fig. 13A). The growth seems to be episodic with periods of little or no growth followed by renewed precipitation (fig. 13C). This sample shows the effects of system materials in the dark-colored phase that shows a bracket outline (fig. 13D). The scale can aggressively corrode metal components as noted by fragments in early formed scale (fig. 13E). X-ray diffraction (fig. 14) proves the material to be calcium sulfite with gypsum and minor accessory minerals. The diffuse low-angle peak probably represents clay particles.

Clays may play an important but as yet unexamined role in plugging and scale formation. More detailed examination of scale precipitates may show insoluble mineral grains that provide nuclei that initiate deposition. Comparing scale structures, especially the times of nondeposition, to operating details should allow for better operation and more efficient scrubbing. We recommend that petrologic, microprobe, and scanning electron microscope investigations of scrubber scale be undertaken.

Precipitation could even be put to useful work. It should be possible to encourage scavenging of pollutant elements by precipitation in the right parts of the system.

Scale formation can be reduced and SO_x removal increased by adding thiosulfate (Owens and others, 1988) or organic acids (Chi and Lester, 1989; Frandsen and others, 2001).

Evidence exists that the FGD process can also remove fluorine (F), chlorine (Cl), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), lead (Pb), and manganese (Mn), as well as mercury (Hg). The sludge can trap Hg (Kairies and others, 2006), especially in iron or clay phases, but that element is relatively immobile and leaching of Hg from FGD-generated gypsum is unlikely.

Table 10. Dissolution rate (reactivity) and Ca/Mg ratios of Indiana scrubber stone samples

Sample	Dissolution rate	Ca/Mg ratio
Abydel	1.11E-04	20.8
Bainbridge Unit 0	9.99E-05	1.3
Bainbridge Unit 1-3	6.13E-03	90.8
Bainbridge Unit 1-4	9.04E-04	90.8
Bainbridge Unit 1-4 (duplicate)	8.33E-04	82.4
Bainbridge Unit 4	7.99E-04	79.9
Bainbridge Unit 4 (duplicate)	7.89E-04	80.2
Base 0	2.33E-05	-
Bloomington Bench II	9.61E-04	94.1
Bloomington (composite)	8.63E-04	-
Cape Sandy (Paoli)	6.91E-04	-
Cloverdale (composite)	6.55E-04	65.6
Cloverdale Bench II	6.87E-04	77.1
Cloverdale Bench I	7.71E-04	90.0
Columbus Louisville	5.13E-05	1.6
Delphi Bench II	4.80E-05	1.2
Francesville	3.33E-05	1.0
Gosport	3.68E-04	-
IPL Scrubber	6.48E-04	52.4
IPL Scrubber (duplicate)	6.60E-04	53.9
Lowell Mining	8.02E-05	1.1
Lowell Reef Bench III	7.93E-05	1.2
Lowell Reef Bench II	7.13E-05	1.2
Lowell Reef Bench II (duplicate)	7.35E-05	1.2
Lowell Reef Bench I	8.22E-05	1.2
Lowell Reef Composite	7.99E-05	1.2
Mill Town 1 ABC Bench	6.17E-04	56.1
Mill Town 2 ABC Bench	5.71E-04	44.2
Mill Town 4 Bench	3.10E-04	-
Mill Town Bench 3-4 Unit E Bench	1.22E-04	4.6
Mitchell Unit A	6.10E-04	-
Mitchell Unit B	4.66E-04	-

Sample	Dissolution rate	Ca/Mg ratio
Orleans Unit A	5.60E-04	44.4
Orleans Unit X	7.10E-04	74.4
Orleans Unit Y	7.38E-04	72.8
Pipe Creek Jr. East	6.67E-04	75.2
Putnamville Core Unit 3	9.01E-05	3.0
Putnamville Core Unit 1	1.20E-03	79.0
Sieboldt	5.51E-04	-
Spencer	4.63E-04	-
Spencer Composite	4.11E-04	-
Spencer (Scrubber Pile)	4.06E-04	14.1
Spencer (Scrubber Pile duplicate)	4.41E-04	13.9
Stinesville	6.84E-04	70.5
Temple Bench V Unit 8	2.33E-04	25.2
Temple Bench V Unit 7	2.38E-03	10.6
Temple Bench IV Unit 6	3.54E-04	-
Temple Bench IV Unit	1.88E-04	-
Temple Bench III Unit 5	3.29E-04	24.2
Temple Bench III Unit 4	4.63E-05	8.8
Temple Bench III Unit 3	1.74E-04	18.3
Temple Bench II Unit 2	2.46E-03	8.9
Temple Bench I Unit 1	1.78E-04	14.9
Tower Bench III	1.00E-04	14.9
Tower Bench II	8.68E-05	8.0
Tower Bench 0	9.63E-05	4.9

Table 11. Summaries of Indiana limestone samples from PRISM computer model (written commun., Andy Scott, Indianapolis Power and Light Petersburg)

Sample	SO₂ removal (%)	Reagent rate (pounds/min x10⁴)	Utilization (S:Ca ratio)
Bainbridge Unit 1-3	88.9	1.199	93.1
Bainbridge Unit 1-4	89.4	1.123	93.0
Bainbridge Unit 4	89.7	1.094	92.9
Bloomington Bench II	89.1	1.105	93.0
Bloomington Bench I	88.1	1.081	93.5
Campbellsburg	93.2	1.186	92.3
Cloverdale (III) Triplicate	91.3	1.128	92.6
Cloverdale Bench II	89.7	1.106	92.9
Cloverdale Bench (II) Duplicate	89.2	1.124	93.0
Cloverdale Unit Bench I	88.9	1.109	93.1
Columbus	-	-	-
Gosport	90.0	1.084	92.8
Mill Town Bench IV	93.7	1.132	92.3
Mill Town Bench II	89.4	1.077	93.0
Mill Town Bench I	91.1	1.109	92.6
Mill Town Unit 2 ABCD	93.1	1.124	92.3
Orleans (A)	89.8	1.070	92.9
Orleans Unit X	89.8	1.075	92.9
Orleans Unit Y	89.9	1.106	92.8
Paoli Cave Stone	98.3	1.365	91.2
Pipe Creek Jr.	89.9	1.099	92.8
Putnamville Unit 1	89.7	1.096	92.9
Temple Unit Bench III	98.3	1.206	91.3

FLUE GAS DESULFURIZATION RESIDUE USES

Large amounts of FGD scrubber sludge is generated in the United States in all systems (approximately 25.4 million tons in 2006 [American Coal Ash Association, 2006]). The SO_x reacts with $CaCO_3$ to produce calcium sulfite ($CaSO_3=2H_2O$). This material has some industrial uses, but usually air is introduced into reaction tanks to oxidize the sulfite to sulfate or gypsum. Gypsum is a very useful material and large amounts of FGD-generated gypsum, commonly known as syngyp, are used to make wallboard or cement. In 2007 more than 1.2 million tons of Indiana syngyp was used for wallboard. Some use as flowable fill is possible and agricultural use is a potential market. Some sludges have cementaceous properties. FGD sludges, usually mixed with fly ash, have been used successfully in civil engineering applications. Koukouzas and Vasilatos (2008) presented data about syngyp and showed its suitability for various uses. Table 12 gives major uses for FGD gypsum.

Five sites are known to produce synthetic gypsum in Gibson, Jasper, Pike, Porter, and Warrick Counties (Kathryn R. Shaffer, Indiana Geological Survey, written commun., 2008) (Table 13). The Indianapolis Power and Light plant at Petersburg produces sulfite and gypsum (Wolsiffer and Wedig, 1997). Syngyp is used in conventional gypsum products and as a cementaceous material when mixed with coal ash. The Rockport plant did produce at one time a high-brightness sulfite for filler use, but that operation is no longer active. Hower and others (1997) noted that coal feed and operating conditions affect FGD properties and that potential for byproduct uses need examination.

FGD residues can provide alkaline materials, especially calcium, to increase soil pH, and trace elements contained in FGD (such as magnesium, potassium, zinc, or copper) can promote plant or animal growth. The material can also improve physical properties of soils and also reduce solubility of phosphorous compounds. Caution should be exercised as boron, arsenic, selenium, or molybdenum can accumulate in plants to bad effects. Clark and others (2001) urged use of FGD products on agricultural lands, but cautioned that more research must be done to assure efficacy and safety of agricultural uses.
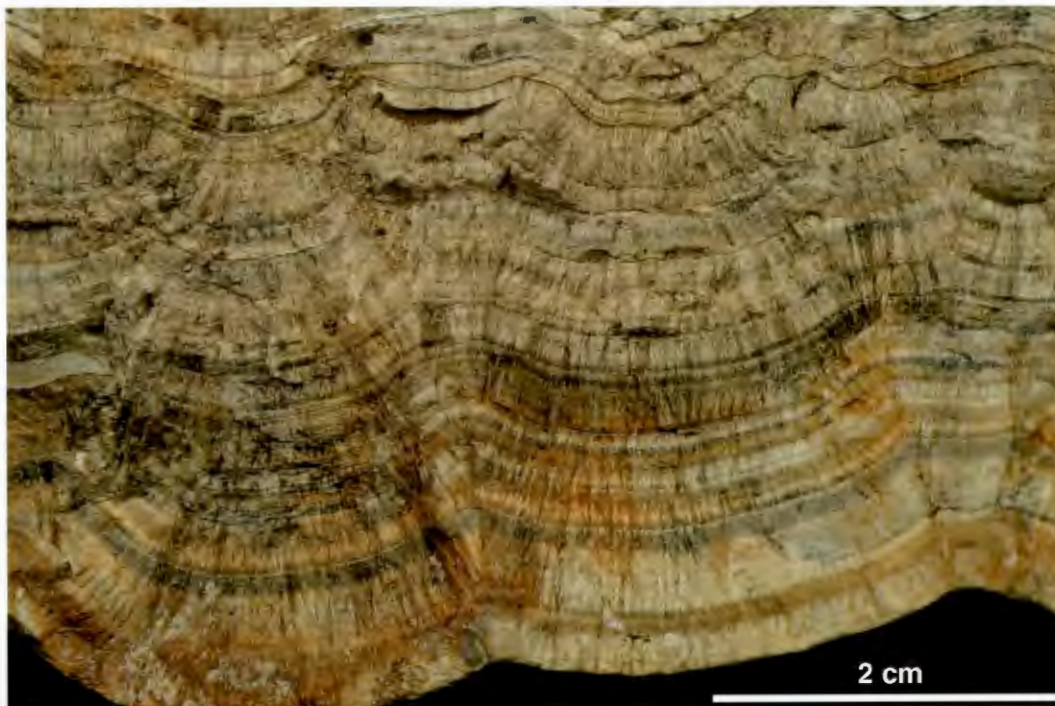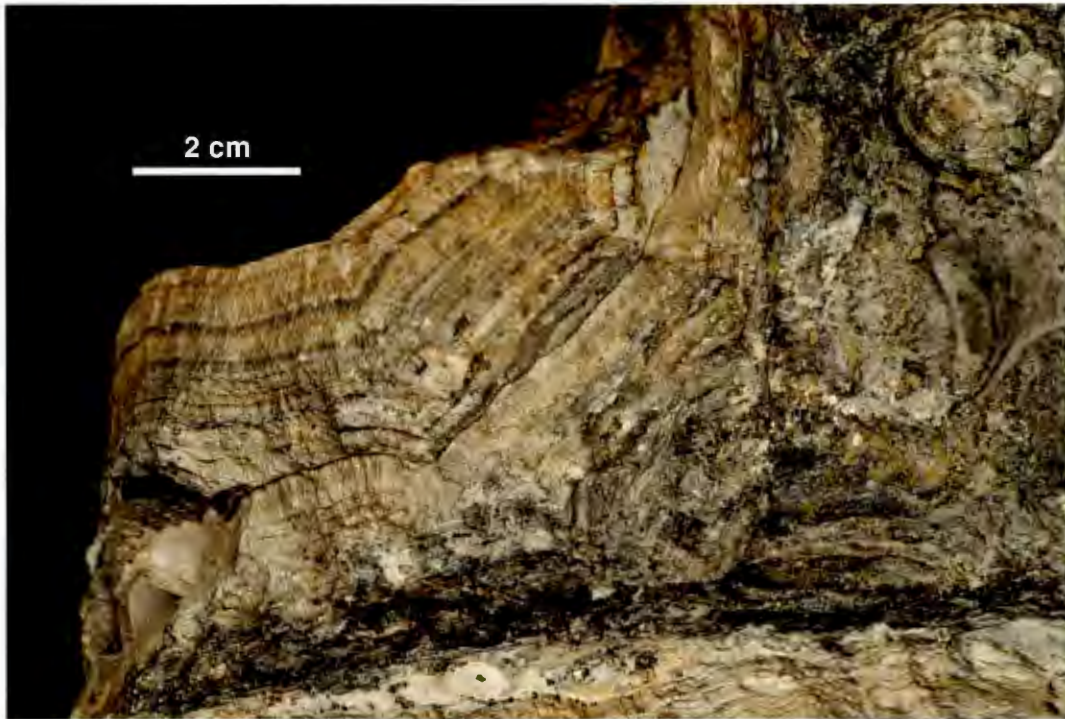
A

B

Figure 13. Photographs of scale formed in wet limestone scrubber. A. Botryoidal scrubber scale mass. These can inhibit scrubber function. B. Scrubber scale forms in concentric layers around metal components of the FGD system.

C

D

Figure 13 (cont.). Photographs of scale formed in wet limestone scrubber. C. Close-up of scale shows fibrous crystals and episodic growth of gypsum. D. Parts of the metal can adhere to scale. Minor phases contain metals.

E

Figure 13 (cont.). Photographs of scale formed in wet limestone scrubber. E. Close-up of D showing metal within early formed scale.

One group applied for a patent to transform FGD sludge into fertilizer (Karras and Jackson, 2003). Kawatra and others (1996) investigated methods to separate and market FGD sulfite, but much remains unknown about sulfites. Other applications are likely.

The basic scrubber sludge calcium sulfite is used as filler in paper and also in various chemical processing steps, especially in wood pulp processing (Scott and others, 1995). Investigation of sulfite properties with an eye toward existing or new uses should be undertaken. Sulfite is also used for soil conditioning and has biocidal properties (Ritchey and others, 1995; Lee and others, 2007).

CONCLUSIONS

Excellent sources of limestone exist in Indiana. Data in this report show that some sources can provide good raw material for wet scrubbing applications. Relatively soft or easily ground stones occur in the Salem and Ste. Genevieve Limestones. Oolitic beds in the Ste. Genevieve show lower specific

Table 12. Uses for flue gas desulfurization residue

Construction materials	
Wallboard	Cement
Woodchip board	Plaster
Civil engineering	
Structural fill	Subsidence control
Flowable fill	Compaction/stabilization
Low permeability cap	
Environmental	
Neutralization	Encapsulation
Erosion/runoff/control	AMD control
Impermeable barrier	Landfill
Agricultural	
Plant nutrient	pH control
Synthetic soil	Crust reduction
Additive for acidic soil	Feedlots/pads
Manufacturing	
Glass	Fertilizer
Pigment	Tile
Filler	Sulfite uses
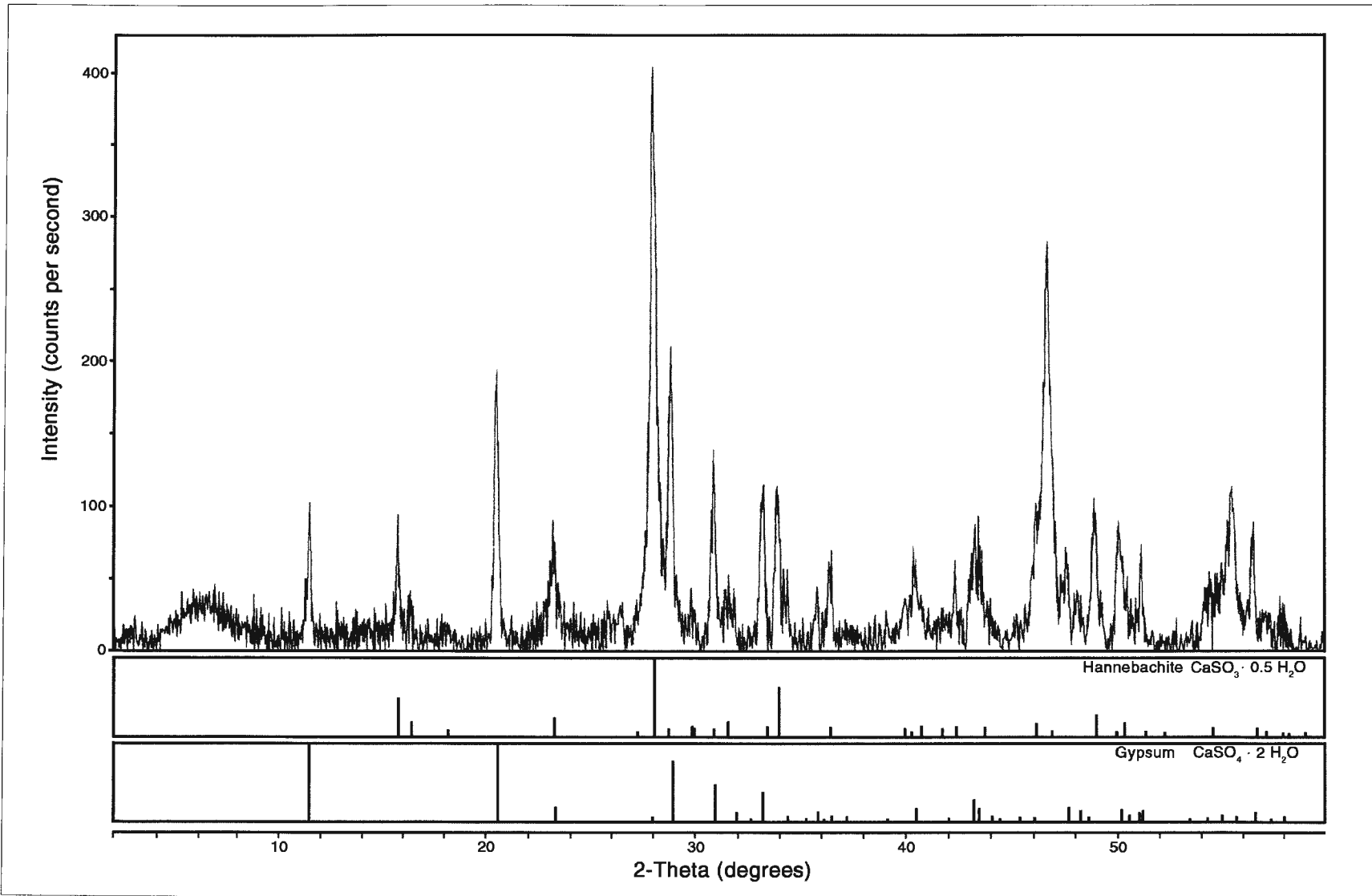
Figure 14. X-ray diffractogram of scale.

Table 13. Indiana flue gas desulfurization byproduct gypsum (syngyp) sold to produce wallboard in 2007*

Company name	Station name	County
Indianapolis Power & Light Co.	Petersburg	Pike
Northern Indiana Public Service Co.	Bailly	Porter
Northern Indiana Public Service Co.	Schahfer	Jasper
Duke Energy Corp.	Gibson	Gibson
Vectren Corp.	F. B. Culley	Warrick

* Indiana FGD byproduct gypsum sold for wallboard in 2007 totaled about 1.2 million short tons.

gravity values and higher porosity values. Nonreactive acid-insoluble residues in pure stones were low at 1 percent to 3 percent.

In addition to good physical properties, several stones have excellent chemical properties. Pure limestones averaging more than 96 percent calcite are present in the Salem, Ste. Genevieve, and Paoli Limestones. Silica as abrasive quartz or nonreactive clays are generally low in these units but quartz does occur in several beds of the Ste. Genevieve Limestone. Clay minerals, which can cause plugging problems, are generally dispersed and rarely occur in levels above 1 percent. They tend to be concentrated in thin beds and could be eliminated, in most instances, by selective benching. Calcium-to-magnesium ratios varied depending on the amount of the mineral dolomite. In FGD systems dolomite reacts less quickly and completely than calcite. Dolomite makes up most samples of rock from the Wabash Formation and so renders them largely unsuitable for FGD uses, but local areas with pure limestone (for example, the Pipe Creek Jr. Quarry in Grant County) can produce good scrubber stone. Parts of the St. Louis Limestone and Muscatatuck Group section contain dolomite and were not sufficiently reactive to be considered for conventional wet scrubbing. Dissolution rates varied by two orders of magnitude with Salem, Ste. Genevieve, and Paoli Limestones showing best dissolution properties.

Computer simulations for 50 data sets yielded estimates for the 22 best samples. These samples should remove 88 to 98 percent of SO_2 at a stone usage rate of 1.07 to 1.36 x 10^4 pounds per minute. Limestone usage as measured by S/Ca ratios averaged 92.6 percent. Salem Limestone, Ste. Genevieve, and Paoli Limestones provide the best scrubber stone characteristics.

Limestone and lime used for wet FGD at electric power stations in Indiana was more than 2 million short tons in 2006. Demand is expected to increase. Byproduct gypsum made from FGD residue, produced by five companies, amounted to more than 1.2 million tons in 2007 (Kathryn Shaffer, Indiana Geological Survey, written commun., 2008).

Increasing byproduct uses should result in improved scrubber economics. Details about stone properties and how they relate to scrubbing efficiency, scale formation, removal of metal pollutants, byproduct formation, and specifications need to be investigated. Limestones suitable for dry scrubbing, fluidized bed, and other SO_x removal techniques undoubtedly occur. Properties useful for those technologies should also be determined.

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